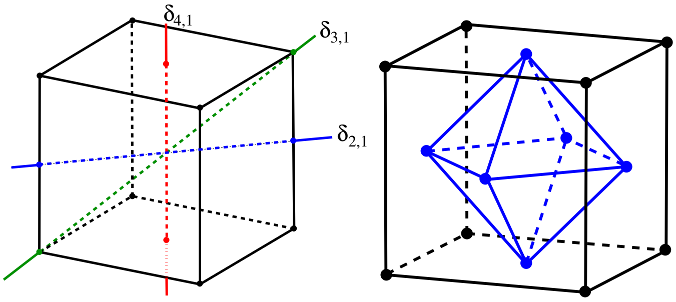

Figure 3.5: left: 3 of the 13 rotational axes that leave a cube unchanged; right:the centers of a cube's faces form a regular octahedron.

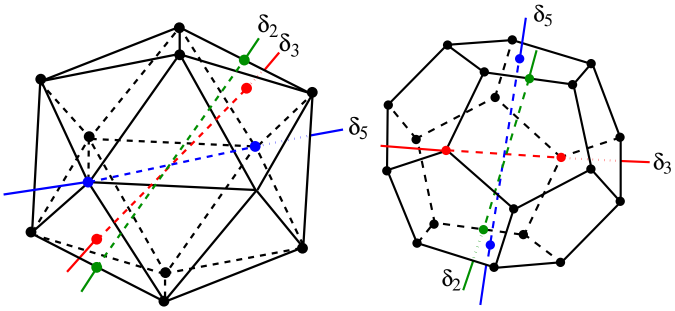

Figure 3.6: left: icosahedron; right: dodecahedron

Icosahedron Group Y

?⟨nams23⟩? The final point group of the first kind is the *Icosahedron Group* Y, which comprises all rotations that leave a regular icosahedron unchanged. An icosahedron is a body with 20 equilateral triangles as faces, as shown in Figure 3.6 (left). The 120 elements of Y consist of:

i) 15 two-fold axes $\delta_{2,i}$ $(i = 1, \ldots, 15)$ through the centers of opposite edges.

ii) 10 three-fold axes $\delta_{3,i}$ $(i = 1, \ldots, 10)$ through opposite vertex corners and faces.

iii) 6 five-fold axes $\delta_{5,i}$ $(i = 1, \ldots, 6)$ through the centers of opposite faces.

The group Y is isomorphic to the symmetry group of a dodecahedron, as depicted in Figure 3.6 (right). However, the icosahedron group does not occur in solids, as we will demonstrate in the next section, so we will not elaborate on it further here.

3.3 Point Groups in Solids

⟨skt57⟩ Before we discuss the point groups of the 2nd kind, we want to prove an important theorem: In crystalline solids, n-fold rotations can be symmetry transformations only if $n = 2, 3, 4$, or 6.
Proof:

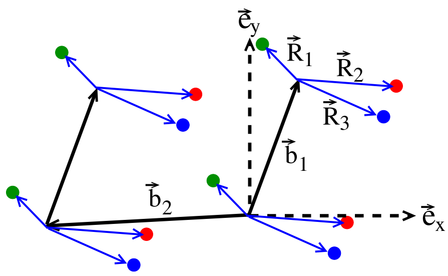

Figure 3.7: Example of a Bravais lattice in 2 dimensions. The Bravais lattice is defined by the vectors $\vec{b}_i$. The vectors $\vec{R}_i$ define a basis at each Bravais lattice site.

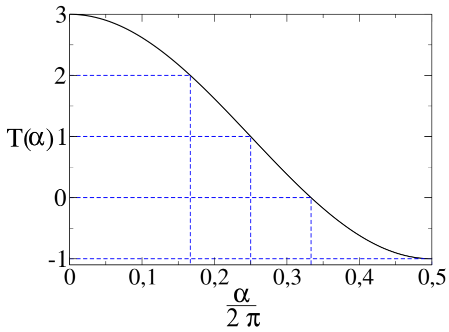

Figure 3.8: Solid line: the function (3.5); dashed lines: the points where the function takes integer values.

do indeed occur in some lattices. The point groups of the first kind that satisfy (3.6) are listed as follows:

$$C_1, C_2, C_3, C_4, D_2, C_6, D_3, D_4, D_6, T, O \ . \qquad (3.7)$$ zuyt

It was previously shown in Section 3.1 that any improper rotation can be expressed as a product of a proper rotation and the inversion. Since the inversion is always a symmetry of a Bravais lattice, the angles (3.6) are also the only possible ones that can occur in the rotational part of improper rotational symmetries in solids.

3.4 The Point Groups of the Second Kind

⟨ansh57⟩ If G is an improper point group, then its sub-group G_0 consisting of proper rotations is a normal sub-group of G with index 2. This means that there exist two cosets, G_0 and L_0, where L_0 contains all the improper rotations.

Proof:

Demonstrating that G_0 and L_0 have equal numbers of elements would be sufficient to establish their index as $j = g/g_0 = 2$. Since E is always an element of G_0, the latter cannot be empty. Let $\tilde{O}$ be an element of L_0. Then, we have

$$\{\underbrace{\tilde{O} \cdot G_0}_{=L_0}, \underbrace{\tilde{O} \cdot L_0}_{=G_0}\} \stackrel{(2.4)}{=} G \ ,$$

because the elements $\tilde{O} \cdot G_0$ and $\tilde{O} \cdot L_0$ have determinants -1 and $+1$ respectively. This proves the above statement. $\surd$

It should be noted that the inversion itself may not be a member of L_0. For instance, in a tetrahedron, there are mirror planes in addition to the rotational axes, but the inversion is not a symmetry operation. In the following sections, we will examine improper point groups that either include or exclude the inversion.

3.4.1 Improper Point Groups without the Inversion

⟨anx109⟩ As we will demonstrate now, improper point groups that do not include the inversion are isomorphic to one of the proper point groups already introduced in Section 3.2, making them mathematically identical. In Section 3.5, however, we will provide physical justifications why it is still meaningful to introduce these groups and to distinguish them from their proper counterparts.

Proof:

We decompose the improper point group (as above),

$$G = \{G_0, L_0\} \ ,$$

Order	Abstract point group	Point groups of the 1. kind	Point groups of the 2. kind with I	Point groups of the 2. kind without I
1	C_1	C_1 [1]		
2	C_2	C_2 [2]	C_i $[\bar{1}]$	C_s $[m]$
3	C_3	C_3 [3]		
4	C_4	C_4 [4]		S_4 $[\bar{4}]$
4	D_2	D_2 [222]	C_{2h} $[\frac{2}{m}]$	C_{2v} $[2mm]$
6	C_6	C_6 [6]	S_6 $[\bar{3}]$	C_{3h} $[\bar{6}]$
6	D_3	D_3 [32]		C_{3v} $[3m]$
8	D_4	D_4 [422]		C_{4v} $[4mm]$, D_{2d} $[\bar{4}2m]$
8	$C_4 \times C_2$		C_{4h} $[\frac{4}{m}]$	
8	$D_2 \times C_2$		D_{2h} $[\frac{2}{m}\frac{2}{m}\frac{2}{m}]$	
12	D_6	D_6 [622]	D_{3d} $[\bar{3}\frac{2}{m}]$	C_{6v} $[6mm]$, D_{3h} $[\bar{6}m2]$
12	T	T [23]		
12	$C_6 \times C_2$		C_{6h} $[\frac{6}{m}]$	
16	$D_4 \times C_2$		D_{4h} $[\frac{4}{m}\frac{2}{m}\frac{2}{m}]$	
24	O	O [432]		T_d $[\bar{4}3m]$
24	$D_6 \times C_2$		D_{6h} $[\frac{6}{m}\frac{2}{m}\frac{2}{m}]$	
24	$T \times C_2$		T_h $[\frac{2}{m}\bar{3}]$	
48	$O \times C_2$		O_h $[\frac{4}{m}\bar{3}\frac{2}{m}]$	

Table 3.2: The 32 inequivalent point groups in solids

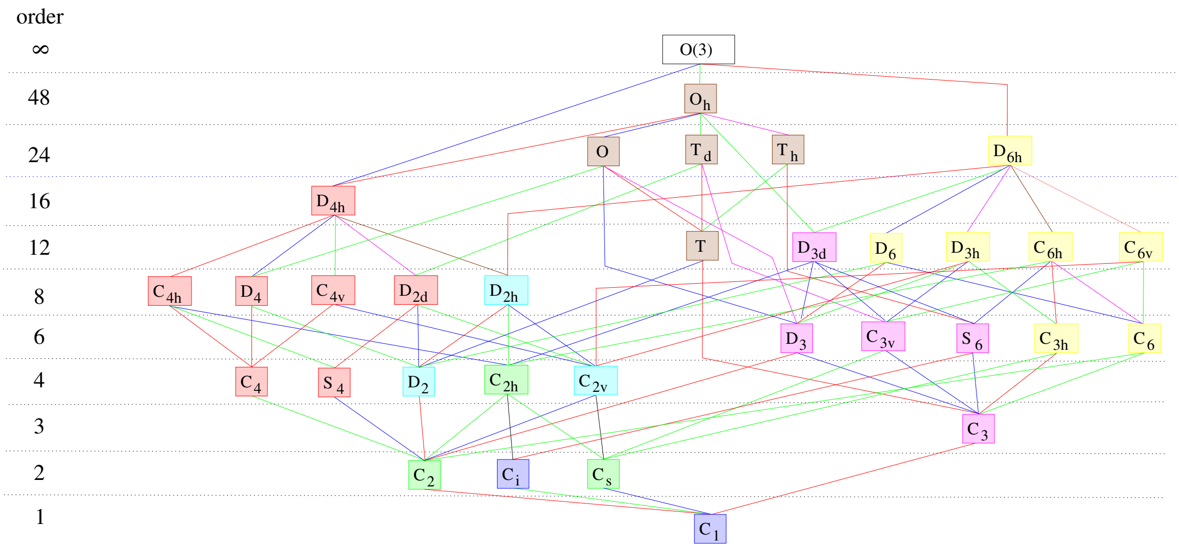

Figure 3.9: The sub-group relationships of the 32 point groups in solids.

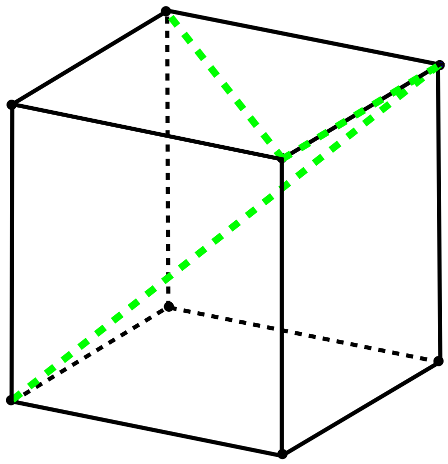

Figure 3.13: Cubic unit cell and the three lines (in green and dashed) on which the additional atom is brought.

i) square,
ii) rectangle,
iii) equilateral triangle,
iv) isosceles triangle,

in the plane perpendicular to it?

5. Create molecules which have the (maximum) symmetry groups

   i) D_2 ,
   ii) D_{3h}.

   There is obviously an infinite number of solutions here.

6. Which of the 32 point groups can be found in every effectively two-dimensional system in solids?

7. Suppose an atom is situated at the center of a cubic box, such that its symmetry group is O_h. How does the symmetry group change when the cube is stretched symmetrically along one of its diagonals?

⟨9764⟩

8. Show that two equivalent point groups are isomorphic.

9. Is the product group $C_2 \times C_4$ isomorphic to C_8?

Given this result, we can proceed with the second step of the proof assuming that $\bar{D}$ forms a unitary matrix group.

ii) Let $\underline{V}^{d'}$ be a non-trivial subspace of $\bar{D}$ which is spanned by the orthonormal basis $\vec{b}_1, \ldots, \vec{b}_{d'}$, while the space orthogonal to $\underline{V}^{d'}$ is spanned by $\vec{c}_{d'+1}, \ldots, \vec{c}_d$. If we represent the matrices $\tilde{D}_i$ in this basis, we find the matrix element

$$\vec{c}_l^{\,\dagger} \cdot \underbrace{\tilde{D}_i \cdot \vec{b}_{l'}}_{\equiv \vec{b} \in \underline{V}^{d'}} = \vec{c}_l^{\,\dagger} \cdot \vec{b} = 0 \quad (\forall l, l') \ .$$

In the last step we have used that $\vec{c}_l^{\,\dagger} \cdot \vec{b}$ is the inner product in a complex vector space and $\vec{c}_l$ is orthogonal to all $\vec{b}_{l'}$ and therefore also to $\vec{b}$. To determine the opposite matrix elements $\vec{b}_l^{\,\dagger} \cdot \tilde{D}_i \cdot \vec{c}_{l'}$ we first transpose it (recall that the transpose of a number is invariant),

$$\vec{b}_l^{\,\dagger} \cdot \tilde{D}_i \cdot \vec{c}_{l'} = \vec{c}_{l'}^{\,\mathrm{T}} \cdot \tilde{D}_i^{\mathrm{T}} \cdot \left(\vec{b}_l^{\,\dagger}\right)^{\mathrm{T}} = (\vec{c}_{l'}^{\,\dagger} \cdot \tilde{D}_i^{\dagger} \cdot \vec{b}_l)^* \ . \qquad (4.8) \quad \text{nsw}$$

Now we use the unitarity of $\tilde{D}_i$,

$$\vec{c}_{l'}^{\,\dagger} \cdot \tilde{D}_i^{\dagger} \cdot \vec{b}_l = \vec{c}_{l'}^{\,\dagger} \cdot \underbrace{\tilde{D}_i^{-1} \cdot \vec{b}_l}_{\equiv \vec{b} \in \underline{V}^{d'}} = \vec{c}_l^{\,\dagger} \cdot \vec{b} = 0 \quad (\forall l, l') \ ,$$

which proves that (4.8) vanishes. With this result, we have shown that after a basis transformation into the basis $\vec{b}_1, \ldots, \vec{b}_{d'}, \vec{c}_{d'+1}, \ldots, \vec{c}_d$, every matrix is block diagonal (i.e. $\bar{D}$ is reducible) in contradiction to the assumption. $\surd$

Schur's Lemma, Part One

?⟨audgtcv⟩? Suppose we have two irreducible matrix groups, $\bar{D}$ and $\bar{D}'$, with the same order g but, in general, different dimensions d and d'. If there exists a $(d \times d')$-dimensional matrix $\tilde{S}$ such that

$$\tilde{S} \cdot \tilde{D}_i' = \tilde{D}_i \cdot \tilde{S} \quad \forall i \ , \qquad (4.9) \quad \text{xbhst}$$

then it is either

i) $\tilde{S} = \tilde{0}$, or

ii) $\tilde{S}$ is square and non-singular, i.e. $\bar{D}$ and $\bar{D}'$ are equivalent.

Proof:

i) Let $\vec{s}_k$ be the d' columns of $\tilde{S}$ and $\underline{V}^{\bar{d}}$ $(\bar{d} \leq d)$ the space spanned by all $\vec{s}_k$. As a first step we want to show that it is either $\bar{d} = d$ or $\bar{d} = 0$. Equation (4.9), expressed by the vectors $\vec{s}_k$, has the following form

$$\sum_{k'} (\tilde{D}_i')_{k',k} \vec{s}_{k'} = \tilde{D}_i \cdot \vec{s}_k \qquad (\forall k = 1, \ldots, d') \ . \qquad (4.10) \quad \text{ayte}$$

The left-hand side of Equation (4.10) is evidently an element of $\underline{V}^{\bar{d}}$. Consequently, for all i, $\tilde{D}_i \cdot \vec{s}_k$ must also be in $\underline{V}^{\bar{d}}$. Thus, either $\bar{d} = d$ or $\bar{d} = 0$, as otherwise there would exist a non-trivial subspace that is invariant under all $\tilde{D}_i$, which contradicts the irreducibility of $\tilde{D}_i$. We shall examine both possibilities:

a) When $\bar{d} = d$, it follows that $d' \geq d$ since d' vectors $\vec{s}_k$ cannot span a d-dimensional vector space $\underline{V}^d$.

b) If $\bar{d} = 0$ it must be $\tilde{S} = \tilde{0}$.

ii) If we take the adjoint of Equation (4.9) and follow the same arguments as in case ii), we obtain either $\bar{d} = d'$, which implies $d \geq d'$, or $\tilde{S} = \tilde{0}$. Here we have used the fact that, if $\bar{D}$ is an irreducible matrix group, then its adjoint group $\bar{D}^\dagger \equiv \{\tilde{D}_1^\dagger, \ldots, \tilde{D}_g^\dagger\}$ is also irreducible.

The results from i) and ii) combined mean that it is either $d = d' = \bar{d}$ (and $\tilde{S}$ is then non-singular) or $\tilde{S} = \tilde{0}$. $\surd$

Schur's Lemma, Part Two

?⟨1jd56xc⟩? Let $\bar{D}$ be an irreducible matrix group. If there is a square matrix $\tilde{S} \neq \tilde{0}$ which commutes with all $\tilde{D}_i \in \bar{D}$,

$$\tilde{D}_i \cdot \tilde{S} = \tilde{S} \cdot \tilde{D}_i \quad \forall i \; ,$$

then $\tilde{S}$ is a multiple of the identity matrix,

$$\tilde{S} = \lambda \cdot \tilde{1} \; . \tag{4.11}$$ akie

Proof:
Let $\lambda \in \mathbb{C}$ be an eigenvalue of $\tilde{S}$. Then $\tilde{S}' \equiv \tilde{S} - \lambda \cdot \tilde{1}$ also commutes with all $\tilde{D}_i$. However, $\tilde{S}'$ is singular, and therefore it is $\tilde{S}' = \tilde{0}$ because of the first part of Schur's lemma, which proves Equation (4.11). $\surd$

4.2 Representations

⟨qyyrt⟩ Representations of groups play a crucial role in establishing the relationship between group theory and its applications in physics. Let G be a group and $\bar{\Gamma}$ a matrix group. If there exists a homomorphic map $f : G \to \bar{\Gamma}$, then f is said to be a representation of G. By definition, a homomorphic map satisfies the following condition:

$$\tilde{\Gamma}(a \cdot b) = \tilde{\Gamma}(a) \cdot \tilde{\Gamma}(b) \qquad \forall \; a, b \in G \; . \tag{4.12}$$ oatqy

For those new to this field, it can be confusing that the same term 'representation' is used for both the map f itself and the image of the map, which is the matrix group $\bar{\Gamma}$.

To get a first impression of the concept of representations of groups, we introduce some additional definitions and remarks:

i) A representation is not necessarily bijective, i.e. two elements $a \neq b \in G$ can be assigned the same matrix. For example,

$$\tilde{\Gamma}(a) = \tilde{1} \qquad \forall \; a \in G \; ,$$

is always a representation (with matrices $\tilde{1}$ of arbitrary dimension). The special case that $\tilde{1} = 1$ is a number is also referred to as a *one-representation*. We will encounter this representation a few times in later chapters.

ii) If the map f is bijective, the representation $\bar{\Gamma}$ is isomorphic to G and is then called *faithful*. This means that in the case of point groups, the three-dimensional matrices that define such a group can also be interpreted as representations of themselves. This will indeed become relevant, e.g. in Chapter 9.

where the matrix elements $\Gamma^{(\mathrm{r})}_{l,j}(a_i)$ for a fixed j, i are non-zero (and equal to 1) for exactly one value of l and the sum sign, as has often been the case, has the meaning of a union of sets. The matrices $\tilde{\Gamma}(a_i)$ form the (faithful) so-called *regular representation* $\bar{\Gamma}^{(\mathrm{r})}$ of G. For example, the regular representation matrices of D_2 are (compare the multiplication Table 2.3) $\tilde{\Gamma}^{(\mathrm{r})}(E) = \tilde{1}$ and

$$\tilde{\Gamma}^{(\mathrm{r})}(\delta_{2x}) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \;,\; \tilde{\Gamma}^{(\mathrm{r})}(\delta_{2y}) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \;,\; \tilde{\Gamma}^{(\mathrm{r})}(\delta_{2z}) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \;.$$

Proof (of the previous statement):
We prove successively the representation property and the isomorphism

i) To show that $\bar{\Gamma}^{(\mathrm{r})}$ is a representation, we multiply Equation (4.17) from the left with another element a_k,

$$\begin{aligned} a_k \cdot (a_i \cdot a_j) &\overset{(4.17)}{=} \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot a_k \cdot a_l \overset{(4.17)}{=} \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot \sum_m \Gamma^{(\mathrm{r})}_{m,l}(a_k) \cdot a_m \\ &= \sum_m \Big[\sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot \Gamma^{(\mathrm{r})}_{l,j}(a_i) \Big] \cdot a_m \;. \end{aligned} \qquad (4.18) \; \texttt{sddff}$$

The brackets on the left side of this equation are, of course, meaningless because of the associative law and it is equal to

$$(a_k \cdot a_i) \cdot a_j \overset{(4.17)}{=} \sum_m \Big[\Gamma^{(\mathrm{r})}_{m,j}(a_k \cdot a_i) \Big] \cdot a_m \;. \qquad (4.19) \; \texttt{sddffb}$$

A comparison of (4.18) and (4.19) then proves that

$$\tilde{\Gamma}^{(\mathrm{r})}(a_k \cdot a_i) = \tilde{\Gamma}^{(\mathrm{r})}(a_k) \cdot \tilde{\Gamma}^{(\mathrm{r})}(a_i) \;.$$

ii) If G and $\bar{\Gamma}^{(\mathrm{r})}$ were not isomorphic there would be at least two elements $a_i \neq a'_i$ with $\tilde{\Gamma}^{(\mathrm{r})}(a_i) = \tilde{\Gamma}^{(\mathrm{r})}(a'_i)$. But then, because of (4.17),

$$a_i \cdot a_j = a'_i \cdot a_j \quad \Rightarrow \quad a_i = a'_i \;,$$

which leads to a contradiction.

Similar to Schur's lemma, we will need the regular representation only in the proofs in Chapter 5, but it will not play a role in the rest of the book.

Theorem 3: The reduced form of the regular representation $\bar{\Gamma}^{(\mathrm{r})}$ of a group G contains each of the irreducible representations $\bar{\Gamma}^p$ of G exactly d_p times, where d_p is the dimension of the irreducible representation $\bar{\Gamma}^p$.

Since the reduced representations have the same dimensions as the original representation (see Equation (4.16)), the following equation results from Theorems 1 and 3

$$g = \sum_{p=1}^{r} d_p^2 \;, \qquad (4.20) \; \texttt{zbhst}$$

5.2 Consequences

⟨vbgft6w9⟩
5.2.1 Theorem 4: Orthogonality of the Characters

??⟨h5hbs⟩? Let $\bar{\Gamma}^p$ be the representations of a group G of order g and χ_i^p its characters. Due to Theorem 1, which we will prove in the following Section 5.2.2, we have $i, p = 1, \ldots, r$, where r is the number of classes of G, as always. Under these conditions, the following two orthogonality theorems hold,

$$g \cdot \delta_{p,q} = \sum_{i=1}^{r} r_i \cdot (\chi_i^p)^* \cdot \chi_i^q \ , \quad (5.9) \ \text{uuat34}$$

$$\frac{g}{r_i} \cdot \delta_{i,j} = \sum_{p=1}^{r} (\chi_i^p)^* \cdot \chi_j^p \ , \quad (5.10) \ \text{uuat34b}$$

where r_i is the number of elements in the i-th class.

5.2.2 Proof of Theorems 1-4:

⟨fghaovcc1⟩ We prove the Theorems 1-4 in 4 steps.

i) We consider only unitary representations $\bar{\Gamma}^p$, which is possible because every representation is equivalent to a unitary one (see Section 4.1.1) and the corresponding character χ^p is invariant under similarity transformations. For each (not necessarily irreducible) representation $\bar{\Gamma}$, we define the r-dimensional character vector

$$\vec{v}^{\Gamma} \equiv \left(\sqrt{\frac{r_1}{g}} \chi_1^{\Gamma}, \ldots, \sqrt{\frac{r_r}{g}} \chi_r^{\Gamma} \right)^T \ . \quad (5.11) \ \text{ogsq}$$

If $\bar{\Gamma} = \bar{\Gamma}^p$ is irreducible, it holds for the associated character vector $\vec{v}^p$ that

$$(\vec{v}^p)^\dagger \cdot \vec{v}^q = \delta_{p,q} \ .$$

To prove this equation, we evaluate the left hand side,

$$(\vec{v}^p)^\dagger \cdot \vec{v}^q \overset{(5.11)}{=} \sum_{i}^{r} \frac{r_i}{g} \cdot (\chi_i^p)^* \cdot \chi_i^q = \frac{1}{g} \sum_{a} (\chi_i^p(a))^* \cdot \chi_i^q(a) \ ,$$

where a are the elements of the group. With the definition (4.15) of the character we then find

$$(\vec{v}^p)^\dagger \cdot \vec{v}^q = \frac{1}{g} \sum_{i=1}^{d_p} \sum_{j=1}^{d_q} \Gamma_{i,i}^p(a^{-1}) \cdot \Gamma_{j,j}^p(a) \overset{(5.1)}{=} \delta_{p,q} \frac{1}{d} \sum_{i=1}^{d_p} = \delta_{p,q} \ . \checkmark \quad (5.12) \ \text{azn6r}$$

Equation (5.12) establishes the validity of Equation (5.9). Conversely, it can be deduced that the maximum number of irreducible representations is r, based on the fact that an r-dimensional space can contain no more than r orthogonal vectors $\vec{v}^p$. In order to prove Theorem 1, it is necessary to demonstrate that there are also at least r irreducible representations, which will bring the total number to exactly r. This will be done in connection with point iii). However, before that, we address Theorem 3.

Then (if $\bar{\Gamma}$ is irreducible) we can deduce from Schur's lemma (part two)

$$\tilde{S}_j = \mu_j \cdot \tilde{1} \; .$$

Especially for the irreducible representations $\bar{\Gamma}^p$ with dimension d_p we find the matrices

$$\tilde{S}_j^p = \mu_j^p \cdot \tilde{1} \; . \tag{5.19}$$ 234r

The trace of the two sides of this equation and

$$\sum_{a \in \mathcal{C}_j} 1 = r_j \; ,$$

yields

$$\mu_j^p = \frac{r_j \chi_j^p}{d_p} \; . \tag{5.20}$$ 234rb

On the other hand, because of the definition of (5.18), it is

$$\tilde{S}_i^p \cdot \tilde{S}_j^p = \sum_{\substack{a \in \mathcal{C}_i \\ b \in \mathcal{C}_j}} \tilde{S}^p(a \cdot b) \overset{(2.7)}{=} \sum_{k=1}^{r} f_{ijk} \cdot \tilde{S}_k \; ,$$

where c_{ijk} are the multiplication coefficients introduced in Section 2.3.3. With Equations (5.19) and (5.20) we find

$$r_i \cdot r_j \cdot \chi_i^p \cdot \chi_j^p = d_p \sum_{k=1}^{r} f_{ijk} \cdot r_k \cdot \chi_k^p \; .$$

Next we carry out the sum over p on both sides and use Equation (5.17),

$$r_i \cdot r_j \sum_p \chi_i^p \cdot \chi_j^p = f_{ij1} \cdot r_1 \cdot g \; .$$

Recall that $r_1 = 1$ and with (2.8) we obtain

$$\sum_p \chi_i^p \cdot \chi_j^p = \frac{g}{r_j} \delta_{i,\bar{j}} \overset{j \to \bar{j}}{\Longrightarrow} \sum_p \chi_i^p \cdot \chi_{\bar{j}}^p = \frac{g}{r_j} \delta_{i,j} \; , \tag{5.21}$$ ki87

where we have used that a class and its inverse have the same number of elements, $r_{\bar{j}} = r_j$. To finish this part of the proof, we have to evaluate $\chi_{\bar{i}}^p$ in (5.21). With $a \in \mathcal{C}_j$ and $a^{-1} \in \mathcal{C}_{\bar{j}}$ we show in Exercise 7 that

$$\chi_{\bar{j}}^p = \left(\chi_j^p\right)^* \; .$$

As a result of this, we can write

$$\sum_p \chi_i^p \cdot \left(\chi_j^p\right)^* = \frac{g}{r_j} \delta_{i,j} \; ,$$

which proves the orthogonality theorem (5.10). Using this equation, we have also demonstrated that in the matrix of character vectors $(\vec{v}^1, \ldots, \vec{v}^{\bar{r}})$, not only are all columns orthogonal, but so are all rows. This implies that the rows must have a minimum dimension of r, meaning there are at least r distinct character vectors. Since we have already established in i) that there can be at most r distinct character vectors, we can now conclude that there are exactly r such vectors. This proves Theorem 1, which states that the number of classes corresponds to the number of irreducible representations.

If $\bar{\Gamma}$ is irreducible, only one n_p in (5.26) is non-zero and equal to 1. In all other cases, the sum over n_p^2 is greater then one. This proves the criterion. $\surd$

Example

As an example, we can now verify that the representations of the group D_3 introduced in Section 4.2 are indeed irreducible. With Table 4.1 we find for the left side of (5.24)

$$\begin{aligned} A_1 &: 1+2+3 = 6(=g) \ , \ \surd \\ A_2 &: 1+2+3 = 6 \ , \ \surd \\ E &: 1\cdot 2^2 + 2\cdot(-1)^2 = 6 \ . \ \surd \end{aligned}$$

Exercises

⟨jjahr⟩

1. Let $G = G_1 \times G_2$ be a product group of two groups

$$\begin{aligned} G_1 &= \{a_1 \ldots, a_{g_1}\} \ , \\ G_2 &= \{b_1 \ldots, b_{g_2}\} \ , \end{aligned}$$

and

$$\begin{aligned} \bar{\Gamma}^1 &= \{\tilde{\Gamma}^1(a_1), \ldots, \tilde{\Gamma}^1(a_{g_1})\} \ , \\ \bar{\Gamma}^2 &= \{\tilde{\Gamma}^2(b_1), \ldots, \tilde{\Gamma}^2(b_{g_2})\} \ , \end{aligned}$$

(not necessarily irreducible) representations of G_1 and G_2.

a) Show that two elements $(a_i; b_j)$ and $(a'_i; b'_j)$ of G are in a class (i.e. $(a_i; b_j) \sim (a'_i; b'_j)$) if, and only if $a_i \sim a'_i$ in G_1 and $b_j \sim b'_j$ in G_2. What classes are there in $G = G_1 \times G_2$ and how many elements does each class have?

b) Show that the product matrices

$$\Gamma^{1\otimes 2}_{(ij),(kl)}((a_n; b_m)) \equiv \Gamma^1_{i,k}(a_n) \cdot \Gamma^2_{j,l}(b_m)$$

are a representation of the group G (*product representations*).

c) Show that $\bar{\Gamma}^{1\otimes 2}$ is irreducible if $\bar{\Gamma}^1$ and $\bar{\Gamma}^2$ are irreducible (use the result from Section 5.2.3).

2. Using the result from Exercise 1, determine the irreducible representations of

$$D_{3d} = D_3 \times (E, I) \ .$$

Use the fact that (E, I) is isomorphic to C_2 (see Table 6.1) and the irreducible representations of D_3 (see the example in Section 4.2).

⟨laqre⟩

3. It is evident that a group comprising of orthogonal matrices,

$$G = \{\tilde{D}_1, \ldots, \tilde{D}_g\} \ ,$$

forms a (real, faithful) three-dimensional representation of the corresponding (abstract) point group (as explained in Section 3.5). This representation, however, is typically reducible. Determine the irreducible components of these representations for the groups D_2 and D_3.

Hint: A helpful approach is to employ Equation (5.23) in combination with the character tables 5.1.

6.1.2 Representation Functions of Irreducible Representations

⟨df70⟩ The d basis functions of a d-dimensional irreducible representation $\bar{\Gamma}^p$ form an orthogonal function system.
Proof
We consider the scalar product of two basis functions $|\lambda\rangle$, $|\mu\rangle$,

$$\langle\lambda|\mu\rangle = \frac{1}{g}\sum_{a\in G}\langle\lambda|\hat{U}_a^\dagger \cdot \hat{U}_a|\mu\rangle \ ,$$

where we have used that

$$1 = \hat{U}_a^\dagger \cdot \hat{U}_a = \frac{1}{g}\sum_{a\in G}\hat{U}_a^\dagger \cdot \hat{U}_a \ .$$

With Equation (6.1) we then find

$$\langle\lambda|\mu\rangle = \frac{1}{g}\sum_{\lambda',\mu'}\sum_{a\in G}\left(\Gamma^p_{\lambda',\lambda}(a)\right)^* \cdot \Gamma^p_{\mu',\mu}(a)\cdot\langle\lambda'|\mu'\rangle \stackrel{(5.2)}{=} \frac{1}{d}\delta_{\lambda,\mu}\sum_{\lambda'}\langle\lambda'|\lambda'\rangle \sim \delta_{\lambda,\mu} \ . \ \checkmark$$

In the following, we assume that the representation functions are normalized. The representation functions of a d-dimensional representation $\bar{\Gamma}$ form a basis for a d-dimensional subspace $\underline{V}^d$ of the Hilbert space $\underline{H}$. This subspace is referred to as the representation space of $\bar{\Gamma}$. It is possible for a representation to have multiple representation spaces, which may be infinite in number. For instance, there exists an infinite set of states of the form (6.3), since there are infinitely many functions $f(|\vec{r}|)$ that can be chosen to be orthogonal. On the other hand, a representation space uniquely determines the corresponding representation (up to equivalence).
Proof
Let Equation (6.1) be satisfied. Then we choose another basis $|\lambda\rangle_2$ of the representation space, thus

$$|\lambda\rangle_2 = \sum_{\lambda'}U_{\lambda',\lambda}|\lambda'\rangle \ .$$

Then,

$$\hat{U}_a|\lambda\rangle_2 = \sum_{\lambda'}U_{\lambda',\lambda}\cdot\hat{U}_a|\lambda'\rangle \stackrel{(6.1)}{=} \sum_{\lambda',\mu'}U_{\lambda',\lambda}\cdot\Gamma_{\mu',\lambda'}|\mu'\rangle \ .$$

We can now also express the state $|\mu'\rangle$ in reverse by $|\mu\rangle_2$,

$$|\mu'\rangle = \sum_{\mu}\left(\tilde{U}^{-1}\right)_{\mu,\mu'}|\mu\rangle_2 \ .$$

This leads to

$$\hat{U}_a|\lambda\rangle_2 = \sum_{\mu}\Gamma'_{\mu,\lambda}|\mu\rangle_2 \ ,$$

with

$$\bar{\Gamma}' = \tilde{U}^{-1}\cdot\bar{\Gamma}\cdot\tilde{U} \ ,$$

which proves the statement.

6.1.3 Representation Spaces and Invariant Sub-spaces

⟨ansg5⟩ It is clear that every representation space is a subspace of $\underline{H}$ that is invariant (as defined in Section 4.1.2) under all operators $\hat{U}_a$. However, the converse is also true: every subspace $\underline{V}^d$ that is invariant under all $\hat{U}_a$ operators is a representation space.

Proof

Let $|\lambda\rangle$ $(\lambda = 1, \ldots, d)$ be a basis of $\underline{V}^d$. Then, the invariance means

$$\hat{U}_a|\lambda\rangle = \sum_{\lambda'} D_{\lambda',\lambda}(a)|\lambda'\rangle \; . \tag{6.4}$$ sdf5

To prove the statement, we need to show the representation properties of the matrices $\tilde{D}(a)$:

$$\begin{aligned} \hat{U}_a \cdot \hat{U}_b|\lambda\rangle &= \sum_{\lambda''} D_{\lambda'',\lambda}(b) \cdot \hat{U}_a|\lambda''\rangle = \sum_{\lambda',\lambda''} D_{\lambda'',\lambda}(b) \cdot D_{\lambda',\lambda''}(a)|\lambda'\rangle \\ &= \hat{U}_{a\cdot b}|\lambda\rangle = \sum_{\lambda'} D_{\lambda',\lambda}(a \cdot b)|\lambda'\rangle \; . \end{aligned}$$

Therefore

$$D_{\lambda',\lambda}(a \cdot b) = \sum_{\lambda''} D_{\lambda',\lambda''}(a) \cdot D_{\lambda'',\lambda}(b) \; . \quad \surd$$

6.1.4 Irreducibility of Representation Spaces

?⟨cv398yq1⟩? If a representation space $\underline{V}^d$ of dimension d can be expressed as a direct sum of two representation spaces of smaller dimension, i.e.

$$\underline{V}^d = \underline{V}^{d_1} \oplus \underline{V}^{d_2} \;\; (d_1 + d_2 = d) \; , \tag{6.5}$$ any6

it is referred to as reducible.

Otherwise, it is called irreducible. The representation corresponding to $\underline{V}^d$ is reducible if and only if $\underline{V}^d$ itself is reducible.

Proof:

We have to give the proof in both directions:

i) We assume that $\underline{V}^d$ is reducible and is spanned by the states $\{|\lambda\rangle\}$. Then we have to show that the representation $\bar{\Gamma}$ defined by the matrices $\tilde{\Gamma}(a)$ with the elements

$$\Gamma_{\lambda',\lambda}(a) \equiv \langle\lambda'|\hat{U}_a|\lambda\rangle \; ,$$

are reducible. Since $\underline{V}^d$ is reducible, there are bases $\{|\mu\rangle\}$ $(\mu = 1, \ldots, d_1)$ and $\{|\mu\rangle\}$ $(\mu = d_1+1, \ldots, d)$ that span representation spaces $\underline{V}^{d_1}$ and $\underline{V}^{d_2}$ with the property (6.5). The two bases are linked via some matrix $\tilde{S}$, i.e.

$$|\lambda\rangle = \sum_{\mu} S_{\mu,\lambda}|\mu\rangle \; . \tag{6.6}$$ ajhd5

The assumption that the bases are orthogonal does not limit the generality of the proof. Then, the matrix $\tilde{S}$ is unitary. With this and Equation (6.4) we find $(\tilde{D} \to \tilde{\Gamma})$

$$\langle\lambda|\hat{U}_a|\lambda'\rangle = \Gamma_{\lambda,\lambda'}(a) \overset{(6.6)}{=} \sum_{\mu,\mu'} S^*_{\mu,\lambda} \cdot S_{\mu',\lambda'} \cdot \langle\mu|\hat{U}_a|\mu'\rangle \; .$$

In matrix form, this equation is given by $(\Gamma'_{\mu,\mu'}(a) \equiv \langle\mu|\hat{U}_a|\mu'\rangle)$

$$\tilde{S}^{-1} \cdot \tilde{\Gamma}'(a) \cdot \tilde{S} = \tilde{\Gamma}(a) \;\; \Rightarrow \;\; \tilde{\Gamma}'(a) = \tilde{S} \cdot \tilde{\Gamma}(a) \cdot \tilde{S}^{-1} \; .$$

Since $\bar{\Gamma}'$ is block diagonal, $\bar{\Gamma}$ is reducible. $\surd$

The states $|p,m,\lambda\rangle$ with fixed p, m and $\lambda = 1,\dots,d_p$ span an irreducible representation space of G, as can be seen in the following way

$$\hat{U}_a|p,m,\lambda\rangle = \sum_i U_{i,(p,m,\lambda)} \cdot \hat{U}_a|\Psi_i\rangle \ .$$

Since

$$\hat{U}_a|\Psi_i\rangle = \sum_j \Gamma_{j,i}(a)|\Psi_j\rangle \stackrel{(6.10)}{=} \sum_j \sum_{p',m',\lambda'} \Gamma_{j,i}(a)\cdot U^*_{j,(p',m',\lambda')}|p',m',\lambda'\rangle \ .$$

we find

$$\begin{aligned}\hat{U}_a|p,m,\lambda\rangle &= \sum_{p',m',\lambda'} \sum_{i,j} U^*_{j,(p',m',\lambda')}\cdot\Gamma_{j,i}(a)\cdot U_{i,(p,m,\lambda)}|p',m',\lambda'\rangle \\ &\stackrel{(6.9)}{=} \sum_{\lambda'} \Gamma^p_{\lambda',\lambda}|p,m,\lambda'\rangle \ . \surd \end{aligned} \quad (6.11) \text{ shnn56}$$

With Equation (6.10) we can write the state $|\Psi\rangle = |\Psi_1\rangle$ as

$$|\Psi\rangle = \sum_{p,\lambda} \underbrace{\sum_{m=1}^{n_p} U^*_{1,(p,m,\lambda)}|p,m,\lambda\rangle}_{\equiv|\lambda\rangle^p} \ . \quad (6.12) \text{ sjjue}$$

Formally, this creates an expression of the form in Equation (6.7). However, it remains necessary to demonstrate that the state denoted as $|\lambda\rangle^p$ in Equation (6.12) possesses the necessary characteristics. To accomplish this, we must determine the partner functions of $|\lambda\rangle^p$ as

$$|\bar{\lambda}\rangle^p \equiv \sum_{m=1}^{n_p} U^*_{1,(p,m,\lambda)}|p,m,\bar{\lambda}\rangle \ . \quad (6.13) \text{ sjhr5}$$

Note that, on the right-hand side of this equation, the index of $\tilde{U}$ is indeed λ, i.e. the value of λ in $|\lambda\rangle^p$ and not $\bar{\lambda}$ which is the label for the partner functions of $|\lambda\rangle^p$. The states $|\bar{\lambda}\rangle$ (of which $|\lambda\rangle^p$ is one for $\bar{\lambda} = \lambda$) indeed form a representation space, because

$$\begin{aligned}\hat{U}_a|\bar{\lambda}\rangle^p &\stackrel{(6.13)}{=} \sum_{m=1}^{n_p} U^*_{1,(p,m,\lambda)}\cdot\hat{U}_a|p,m,\bar{\lambda}\rangle \\ &\stackrel{(6.11)}{=} \sum_{m=1}^{n_p}\sum_{\bar{\lambda}'} \Gamma^p_{\bar{\lambda}',\bar{\lambda}}\cdot U^*_{1,(p,m,\lambda)}|p,m,\bar{\lambda}'\rangle \stackrel{(6.13)}{=} \sum_{\bar{\lambda}'}\Gamma^p_{\bar{\lambda}',\bar{\lambda}}|\bar{\lambda}'\rangle^p \quad \surd \ .\end{aligned}$$

Before we look at examples of the development theorem, we will first derive a practical way to determine the components in (6.7) in the following section. This is based on the projection operators introduced by Wigner.[1]

6.2 Projection Operators

⟨dgy76z34⟩ Let $\bar{\Gamma}^p$ be the d_p-dimensional (unitary) representations of a group G of unitary operators $\hat{U}_a$ $(p = 1,\dots,r)$. Then, for each p we define the d_p^2 operators

$$\hat{P}^p_{\lambda,\lambda'} \equiv \frac{d_p}{g}\sum_a \left(\Gamma^p_{\lambda,\lambda'}(a)\right)^* \cdot \hat{U}_a \ . \quad (6.14) \text{ dkj67}$$

The following are true

6.3.5 Diagonalization of Hamiltonians

⟨1qazmklo⟩ In practice, one usually diagonalizes a Hamiltonian $\hat{H}$ by choosing a basis $|\varphi_i\rangle$ and then tries to diagonalize the (in general infinite dimensional) Hamiltonian matrix with the elements

$$H_{i,j} = \langle \varphi_i|\hat{H}|\varphi_j\rangle \ ,$$

(in rare cases) analytically or approximately with numerical techniques. Group theory now helps us to find a suitable basis. Let G be the symmetry group of $\hat{H}$ with the r irreducible representations $\bar{\Gamma}^p$. Then, according to the postulate in Section 6.3.3, the Hamiltonian can be written as

$$\hat{H} = \sum_{q,m_q,\lambda_q} E(q,m_q)|q,m_q,\lambda_q\rangle\langle q,m_q,\lambda_q| \ ,$$

with the unknown eigenfunctions $|q,m_q,\lambda_q\rangle$ and eigenvalues $E(q,m_q)$ of $\hat{H}$. We now choose a basis $|\varphi_{p,m,\lambda}\rangle$ of the Hilbert space which consists of orthogonal representation spaces with respect to G with irreducible representations $\bar{\Gamma}^p$ (for example with the projection operators $\hat{P}^p_{\lambda,\lambda}$ introduced in Section 6.2). Then, the matrix elements of $\hat{H}$ with respect to this basis has the form

$$\begin{aligned}\langle \varphi_{p,m_p,\lambda_p}|\hat{H}|\varphi_{p',m_{p'},\lambda_{p'}}\rangle &= \sum_{q,m_q,\lambda_q} E(q,m_q)\langle \varphi_{p,m_p,\lambda_p}|q,m_q,\lambda_q\rangle\langle q,m_q,\lambda_q|\varphi_{p',m_{p'},\lambda_{p'}}\rangle \\ &\overset{6.2.1}{=} \delta_{p,p'}\delta_{\lambda_p,\lambda_{p'}} H^{(p,\lambda)}_{m_p,m_{p'}} \ , \qquad (6.21)\end{aligned}$$ snahyt5

where we have introduced the matrix $\tilde{H}^{(p,\lambda)}$ with the elements

$$H^{(p,\lambda)}_{m,m'} = \langle \varphi_{p,m,\lambda}|\hat{H}|\varphi_{p,m',\lambda}\rangle \ . \qquad (6.22)$$ sjaht3

The diagonalization of $\hat{H}$ is thus reduced to that of the matrices $\tilde{H}^{(p,\lambda)}$. With Equation (6.21), the maximum possible block diagonality due to the symmetry is established. In numerical practice, of course, the procedure introduced here is only worthwhile if $\tilde{H}^{(p,\lambda)}$ can be determined analytically. Applied to the one-dimensional potential in Section 6.3.4, Equation (6.22) reproduces our finding from above that one can diagonalize the Hamiltonian independently in the space of symmetric and antisymmetric wave functions.

Finally, the calculation of the matrix element (6.22) is made even easier by the fact that it is independent of λ, i.e.

$$H^{(p,\lambda)}_{m,m'} = H^{p}_{m,m'} \ . \qquad (6.23)$$ 88uat

Proof

Using Equation (6.18) we find

$$\hat{H} = \hat{U}_a \cdot \hat{H} \cdot \hat{U}^\dagger_a \ ,$$

which we substitute into the matrix element (6.22),

$$\begin{aligned}H^{(p,\lambda)}_{m,m'} = \langle \varphi_{p,m,\lambda}|\hat{H}|\varphi_{p,m',\lambda}\rangle &= \langle \varphi_{p,m,\lambda}|\hat{U}_a \cdot \hat{H} \cdot \hat{U}^\dagger_a|\varphi_{p,m',\lambda}\rangle \qquad (6.24) \\ &\overset{(6.1)/(6.21)}{=} \sum_{\lambda',\lambda''} \Gamma_{\lambda'',\lambda}(a)\left(\Gamma_{\lambda',\lambda}(a)\right)^* \langle \varphi_{p,m,\lambda'}|\hat{H}|\varphi_{p,m',\lambda'}\rangle \ .\end{aligned}$$ sjjhdt

Since the left-hand side does not depend on a, the same must be true for the right-hand side. We can now sum over a on both sides in (6.24), which then leads to

$$\langle\varphi_{p,m,\lambda}|\hat{H}|\varphi_{p,m',\lambda}\rangle = \frac{1}{d_p}\sum_{\lambda'}\langle\varphi_{p,m,\lambda'}|\hat{H}|\varphi_{p,m',\lambda'}\rangle \ .$$

where we used the orthogonality theorem (5.2). Since the right-hand side is independent of λ, the assertion follows. $\surd$

Example

As an example, we consider a rectangular 'molecule' with one orbital per site on which a single quantum mechanical particle is located (see Figure 6.2). The Hamiltonian contains a hopping t, t' to the nearest neighbors which in first quantization reads

$$\hat{H} = \sum_{i,j=1}^{4} t_{i,j}|i\rangle\langle j| \ ,$$

where the values of $t_{i,j}$ are specified in Figure 6.2. In matrix form the Hamiltonian is given as

$$\tilde{H} = \begin{pmatrix} 0 & t' & 0 & t \\ t' & 0 & t & 0 \\ 0 & t & 0 & t' \\ t & 0 & t' & 0 \end{pmatrix} \ .$$

There are obviously 4 symmetry operations, besides the one-element a rotation δ_2 around the z-axis with angle π as well as the two mirror planes σ_1 ($x = 0$) and σ_2 ($y = 0$). Therefore, the symmetry group of the molecule is C_{2v} (see Chapter 3). It has 4 (of course one-dimensional) irreducible representations, which are shown in the character Table 6.2. To use Equation (6.21), we need a basis of representation spaces. We can determine it with the projection operators (6.16). In this case, it is sufficient to take only one of the four states $|i\rangle$ and apply the 4 operators $\hat{P}^p$ to it,

$$\begin{aligned}
\hat{P}^{A_1}|1\rangle &\overset{6.2}{=} \frac{1}{4}\left(\hat{U}_E|1\rangle + \hat{U}_{\delta_2}|1\rangle + \hat{U}_{\sigma_1}|1\rangle + \hat{U}_{\sigma_2}|1\rangle\right) \\
&= \frac{1}{4}\left(|1\rangle + |3\rangle + |2\rangle + |4\rangle\right) \equiv \sqrt{4}|\Psi_{A_1}\rangle \ , \\
\hat{P}^{A_2}|1\rangle &= \frac{1}{4}\left(|1\rangle + |3\rangle - |2\rangle - |4\rangle\right) \equiv \sqrt{4}|\Psi_{A_2}\rangle \ , \\
\hat{P}^{B_1}|1\rangle &= \frac{1}{4}\left(|1\rangle - |3\rangle + |2\rangle - |4\rangle\right) \equiv \sqrt{4}|\Psi_{B_1}\rangle \ , \\
\hat{P}^{B_2}|1\rangle &= \frac{1}{4}\left(|1\rangle - |3\rangle - |2\rangle + |4\rangle\right) \equiv \sqrt{4}|\Psi_{B_2}\rangle \ .
\end{aligned}$$

where the factor $\sqrt{4}$ has been introduced to normalize the 4 states $|\Psi_p\rangle$. These 4 states are orthogonal and therefore form a base of the Hilbert space. Since they belong to different representations, $\hat{H}$ must be diagonal in this basis, i.e. the matrices (6.22) here are one-dimensional with respect to $m_p, m_{p'}$,

$$\begin{aligned}
\tilde{H}' &= \begin{pmatrix} \langle\Psi_{A_1}|\hat{H}|\Psi_{A_1}\rangle & 0 & 0 & 0 \\ 0 & \langle\Psi_{A_2}|\hat{H}|\Psi_{A_2}\rangle & 0 & 0 \\ 0 & 0 & \langle\Psi_{B_1}|\hat{H}|\Psi_{B_1}\rangle & 0 \\ 0 & 0 & 0 & \langle\Psi_{B_2}|\hat{H}|\Psi_{B_2}\rangle \end{pmatrix} \\
&= \begin{pmatrix} t+t' & 0 & 0 & 0 \\ 0 & t-t' & 0 & 0 \\ 0 & 0 & -t+t' & 0 \\ 0 & 0 & 0 & -t-t' \end{pmatrix} \ .
\end{aligned}$$

O_H			E	$6C_4$	$3C_4^2$	$8C_3$	$6C_2'$	I	$3\sigma_h$	$6\sigma_d$	$8S_6$	$6S_4$
$x^2+y^2+z^2=r^2$		$A_{1\mathrm{g}}$	1	1	1	1	1	1	1	1	1	1
		$A_{2\mathrm{g}}$	1	–1	1	1	–1	1	1	–1	1	–1
		$A_{1\mathrm{u}}$	1	1	1	1	1	–1	–1	–1	–1	–1
	xyz	$A_{2\mathrm{u}}$	1	–1	1	1	–1	–1	–1	1	–1	1
$(x^2-y^2, 3z^2-r^2)$		E_g	2	0	2	–1	0	2	2	0	–1	0
		E_u	2	0	2	–1	0	2	–2	0	1	0
		$T_{1\mathrm{g}}$	3	1	–1	0	–1	3	–1	–1	0	1
(zx, yz, xy)		$T_{2\mathrm{g}}$	3	–1	–1	0	1	3	–1	1	0	–1
	(x, y, z)	$T_{1\mathrm{u}}$	3	1	–1	0	–1	–3	1	1	0	–1
	$(x(z^2-y^2),$ $y(z^2-x^2),$ $z(x^2-y^2))$	$T_{2\mathrm{u}}$	3	–1	–1	0	1	–3	1	–1	0	1

Table 7.1: Character table of the group O_H

relevant in solid-state physics. For completeness, we also give the missing representation functions of orders $3-6$ in x, y, z:

$$\begin{aligned} A_{2\mathrm{g}} &: x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)\ , &(7.1)\ \texttt{asdf1} \\ A_{1\mathrm{u}} &: xyz\left[x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)\right]\ , \\ E_{\mathrm{u}} &: xyz\left[(x^2-y^2, 3z^2-r^2)\right]\ , \\ T_{1\mathrm{g}} &: xy(x^2-y^2), xz(x^2-z^2), yz(y^2-z^2)\ . &(7.2)\ \texttt{asdf2} \end{aligned}$$

ii) A convention has been established for the naming of representations:

- One-dimensional representations are labeled as A or B. The difference between A and B denotes the positive or negative character of proper rotations around the main symmetry axis.
- Two- and three-dimensional representations are denoted by E and T, respectively.
- If $I \in G$, the subscript g or u indicates whether the representation is symmetric or antisymmetric under inversion.[3]
- Representations such as A' and A'' differ in their symmetry or antisymmetry relative to the mirror plane perpendicular to the main symmetry axis.[2]

iii) When dealing with groups that have complex-valued characters, it is necessary to analyze their character tables more closely. For instance, consider the group C_4, whose character table is presented in Table 7.2. This group is Abelian, and therefore its four irreducible representations are one-dimensional. However, in accordance with the literature, the character table shows two representations with complex characters that are denoted as two-dimensional. Here we explain why: the functions

$$p_{[x,y]} \equiv f(|\vec{r}|)[x, y]\ ,$$

define a two-dimensional representation space of C_4 with the representation matrices

$$\begin{aligned} \tilde{\Gamma}(E) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\ ,\ \tilde{\Gamma}(C_4) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\ , \\ \tilde{\Gamma}(C_2) &= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}\ ,\ \tilde{\Gamma}(C_4^3) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}\ . \end{aligned}$$

These representation matrices, however, are reducible and can be diagonalized via the transformation

$$\Psi_+ \equiv p_x + \mathrm{ip_y}\ ,\ \ \Psi_- \equiv \mathrm{p_x} - \mathrm{ip_y}\ .$$

In this basis, the representation matrices are

$$\begin{aligned} \tilde{\Gamma}'(E) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\ ,\ \tilde{\Gamma}'(C_4) = \begin{pmatrix} \mathrm{i} & 0 \\ 0 & -\mathrm{i} \end{pmatrix}\ , \\ \tilde{\Gamma}'(C_2) &= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}\ ,\ \tilde{\Gamma}'(C_4^3) = \begin{pmatrix} -\mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix}\ . \end{aligned}$$

These are exactly the two (conjugate complex) one-dimensional representations that we find in the character Table 7.2.

[3]In Exercise 10 of Chapter 5 we show that all representation functions must have one of the two properties.

that are involved then result, as in Section 8.2, from the reduction of $\bar{\Gamma}^p$, i.e. with the help of the respective correlation tables.

Example

To provide an example, we revisit the scenario of a particle in a cubic box discussed in Section 7.2. Specifically, we focus on the first three eigenspaces, which serve as proper representation spaces of an irreducible representation of O_h. We introduce the term $\hat{V} = \alpha\hat{z}^2$ to the system's Hamiltonian, leading to $G_0 = O_h$ and $G = D_4$. As the first eigenspace of $\hat{H}_0$ is non-degenerate, it cannot experience energetic splitting. Consequently, we examine the second and third eigenspaces:

i) The eigenspace $\underline{V}^{[1,1,2]}$ belongs to the representation $T_{1\mathrm{u}}$. According to the correlation Table 8.2 it is

$$T_{1\mathrm{u}} \overset{O_h \to D_{4h}}{\to} A_{2\mathrm{u}} \oplus E_{\mathrm{u}} \ .$$

The states introduced in Section 7.2 are already bases of the spaces $\underline{V}^{A_{2\mathrm{u}}}$ and $\underline{V}^{E_{\mathrm{u}}}$, where

$$\begin{aligned} A_{2\mathrm{u}} &: \Psi_{112} \quad (\sim z) \ , \\ E_{\mathrm{u}} &: \{\Psi_{121}, \Psi_{211}\} \quad (\sim \{x, y\}) \ . \end{aligned}$$

ii) Likewise, the eigenspace $\underline{V}^{[1,2,2]}$ belongs to the representation $T_{2\mathrm{g}}$ and the correlation table yields

$$T_{2\mathrm{g}} \overset{O_h \to D_{4h}}{\to} B_{2\mathrm{g}} \oplus E_{\mathrm{g}} \ ,$$

where

$$\begin{aligned} B_{2\mathrm{g}} &: \Psi_{221} \quad (\sim x \cdot y) \ , \\ E_{\mathrm{g}} &: \{\Psi_{122}, \Psi_{212}\} \quad (\sim \{x \cdot z, y \cdot z\}) \ . \end{aligned}$$

It is crucial to understand the following fact: The splitting of G into irreducible representation spaces $\underline{\tilde{V}}^{p_i}$, which occurs at zeroth order, remains valid beyond the realm of perturbation theory. If this was not the case, there had to be a point where, as $\hat{V}$ steadily increases, a sudden transition into a fundamentally different eigenspace took place. Such a scenario is inconceivable in physical systems, even in the absence of a formal mathematical proof of this statement.

O_h	O	T_d	T_h	D_{4h}	D_{3d}
$A_{1\mathrm{g}}$	A_1	A_1	A_{g}	$A_{1\mathrm{g}}$	$A_{1\mathrm{g}}$
$A_{2\mathrm{g}}$	A_2	A_2	A_{g}	$B_{1\mathrm{g}}$	$A_{2\mathrm{g}}$
$A_{1\mathrm{u}}$	A_1	A_2	A_{u}	$A_{1\mathrm{u}}$	$A_{1\mathrm{u}}$
$A_{2\mathrm{u}}$	A_2	A_1	A_{u}	$B_{1\mathrm{u}}$	$A_{2\mathrm{u}}$
E_{g}	E	E	E_{g}	$A_{1\mathrm{g}} \oplus B_{1\mathrm{g}}$	E_{g}
E_{u}	E	E	E_{u}	$A_{1\mathrm{u}} \oplus B_{1\mathrm{u}}$	E_{u}
$T_{1\mathrm{g}}$	T_1	T_1	T_{g}	$A_{2\mathrm{g}} \oplus E_{\mathrm{g}}$	$A_{2\mathrm{g}} \oplus E_{\mathrm{g}}$
$T_{2\mathrm{g}}$	T_2	T_2	T_{g}	$B_{2\mathrm{g}} \oplus E_{\mathrm{g}}$	$A_{1\mathrm{g}} \oplus E_{\mathrm{g}}$
$T_{1\mathrm{u}}$	T_1	T_2	T_{u}	$A_{2\mathrm{u}} \oplus E_{\mathrm{u}}$	$A_{2\mathrm{u}} \oplus E_{\mathrm{u}}$
$T_{2\mathrm{u}}$	T_2	T_1	T_{u}	$B_{2\mathrm{u}} \oplus E_{\mathrm{u}}$	$A_{1\mathrm{u}} \oplus E_{\mathrm{u}}$

Table 8.2: Correlation table for the group O_h and its largest sub-groups.

8.4 Application: Splitting of Atomic Orbitals in Crystal Fields

⟨pow4xc⟩ Given the orbitals $(s, p, d, \ldots)$ of an atom, the question arises as to what qualitative changes occur when the atom is placed in an environment that is no longer fully rotationally symmetric (e.g. in a solid). To address this, we examine a Hamiltonian of the form

$$\hat{H} = \underbrace{\frac{\hat{\vec{p}}^2}{2m} + V(|\vec{r}|)}_{\text{atom}} + V_{\text{cf}}(\vec{r}) \equiv \hat{H}_0 + V_{\text{cf}}(\vec{r}) \ ,$$

where $V_{\text{cf}}(\vec{r})$ is commonly known as the *crystal field* in solid-state physics. The symmetry group G_0 of H_0 is not finite, which sets it apart from all other groups discussed in this book. However, we can avoid dealing with such infinite (*Lie*) groups in detail by utilizing our understanding of the spectrum of $\hat{H}_0$:

8.4.1 The Atomic Problem

?⟨li7xver⟩? **Remainder: Atomic Spectra**

⟨swrt⟩ We briefly repeat the essential results for the spectrum of $\hat{H}_0$, which are derived in every textbook on quantum mechanics:

It is $[\hat{H}_0, \hat{L}_i] = 0$ for all three components $\hat{L}_i$ of the orbital angular momentum $\hat{\vec{L}}$. One then usually shows that $\hat{\vec{L}}^2$ and $\hat{L}_z$ have common eigenstates $|l, m\rangle$, with $(\hbar = 1)$

$$\begin{aligned} \hat{\vec{L}}^2|l,m\rangle &= l(l+1)|l,m\rangle \qquad l = 0,1,2,\ldots \ , \\ \hat{L}_z|l,m\rangle &= m|l,m\rangle \qquad m = -l, -l+1, \ldots, l-1, l \ . \end{aligned}$$

Since $[\hat{H}_0, \hat{\vec{L}}^2] = 0$ and $[\hat{H}_0, \hat{L}_z] = 0$, we can find common eigenstates of all three operators,

$$\hat{H}_0|n,l,m\rangle = E_{n,l}|n,l,m\rangle \ . \tag{8.4}$$ aany716

With the ladder operators $\hat{L}_\pm$,

$$\hat{L}_\pm|n,l,m\rangle \sim |n,l,m\pm 1\rangle \ ,$$

which also commute with $\hat{H}_0$, it follows, e.g.

$$\begin{aligned} & \hat{L}_\pm\hat{H}_0|n,l,m\rangle = E_{n,l}\hat{L}_\pm|n,l,m\rangle \sim E_{n,l}|n,l,m\pm 1\rangle \\ = \ & \hat{H}_0\hat{L}_\pm|n,l,m\rangle \sim \hat{H}_0|n,l,m\pm 1\rangle = E_{n,l}|n,l,m\pm 1\rangle \ . \end{aligned}$$

Therefore, all states $|n,l,m\rangle$ $(m = -l, \ldots, l)$ have the same energy (as already assumed in 8.4) and there is an $(2l+1)$-fold degeneracy of the spectrum. In real space the eigenfunctions (in spherical coordinates) have the form

$$\Psi_{n,l,m}(r,\theta,\varphi) = R_{n,l}(r)Y_{l,m}(\theta,\varphi) \ ,$$

with the spherical harmonics

$$Y_{l,m}(\theta,\varphi) \sim P_l^m(\cos(\theta))e^{\mathrm{i}m\varphi} \ ,$$

and the *associated Legendre polynomials* $P_l^m(\cos(\theta))$. The exact form of the functions $P_l^m(\cos(\theta))$ and $R_{n,l}(r)$ is irrelevant for our following considerations. The wave functions for the lowest values of l are

i) $l = 0$, s-orbitals:

$$Y_{0,0} \sim \text{const} ,$$

ii) $l = 1$, p-orbitals:

$$Y_{1,\pm 1} \sim \sin{(\theta)} e^{\pm \mathrm{i}\varphi}, \; Y_{1,0} \sim \cos{(\theta)} ,$$

iii) $l = 2$, d-orbitals:

$$Y_{2,\pm 2} \sim \sin^2{(\theta)} e^{\pm 2\mathrm{i}\varphi}, \; Y_{2,\pm 1} \sim \sin{(\theta)} \cos{(\theta)} e^{\pm \mathrm{i}\varphi}, \; Y_{2,0} \sim (3\cos^2{(\theta)} - 1) ,$$

iv) $l = 3$, f-orbitals:

$$\begin{aligned} Y_{3,\pm 3} &\sim \sin{(\theta)}^3 e^{\pm 3\mathrm{i}\varphi}, \; Y_{3,\pm 2} \sim \sin{(\theta)}^2 \cos{(\theta)} e^{\pm 2\mathrm{i}\varphi}, \\ Y_{3,\pm 1} &\sim \sin{(\theta)}(5\cos{(\theta)}^2 - 1) e^{\pm \mathrm{i}\varphi}, \; Y_{3,0} \sim (5\cos{(\theta)}^3 - 3\cos{(\theta)}) . \end{aligned}$$

Group-Theoretical Treatment of the Problem

?⟨ius4xnr⟩? The symmetry group of $\hat{H}_0$ is $O(3)$, which comprises of operators $\hat{U}_{\tilde{D}}$ with arbitrary orthogonal matrices $\tilde{D}$. Our objective is to find the representation matrices and, more importantly, the characters of this group (in order to use again Equation (5.23)). To avoid dealing with infinite groups, we will take a pragmatic approach and make use of the results obtained in Section 8.4.1.

As $O(3)$ represents the maximum symmetry group of $\hat{H}_0$, the functions $Y_{l,m}(\theta, \varphi)$ ($m = -l, \ldots, l$) must form a representation space of dimension $(2l + 1)$ for $O(3)$, as stated by our postulate from Section 6.3.3. This enables us to determine some representation matrices and the corresponding characters.

i) Let $\tilde{D}$ be a matrix that describes a rotation around the z-axis with the angle α. Then obviously

$$\hat{U}_{\tilde{D}} \cdot Y_{l,m}(\theta, \varphi) = e^{-\mathrm{i}\cdot m \cdot \alpha} \cdot Y_{l,m}(\theta, \varphi) .$$

The representation matrix of $\tilde{D}$ is therefore diagonal and given as

$$\tilde{\Gamma}^l(\alpha) = \begin{pmatrix} e^{-\mathrm{i}l\alpha} & & & 0 \\ & e^{-\mathrm{i}(l-1)\alpha} & & \\ & & \ddots & \\ 0 & & & e^{\mathrm{i}l\alpha} \end{pmatrix} .$$

Using the well-known geometric sum formula, we can calculate the character $\chi^l(\alpha)$ as:

$$\chi^l(\alpha) = \sum_{m=-l}^{l} e^{\mathrm{i}\cdot m \cdot \alpha} = \frac{\sin\left[\left(l + \frac{1}{2}\right)\alpha\right]}{\sin\left[\frac{\alpha}{2}\right]} . \tag{8.5}$$ 873y6

It is worth noting that for other axes of rotation, the representation matrices are not diagonal, but the characters remain independent of the axis, as long as the rotation angle α is the same. Since we will only be using these characters in the following, we do not need to consider the representation matrices of other axes of rotation.

ii) As one shows in all textbooks on quantum mechanics, the spherical harmonics behave under inversion $\tilde{I}$ as

$$\hat{U}_{\tilde{I}} \cdot Y_{l,m}(\theta, \varphi) = (-1)^l Y_{l,m}(\theta, \varphi) .$$

which means that

$$\chi^l(I) = (-1)^l (2l + 1) .$$

Then (if $\bar{\Gamma}$ is irreducible) we can deduce from Schur's lemma (part two)

$$\tilde{S}_j = \mu_j \cdot \tilde{1} \; .$$

Especially for the irreducible representations $\bar{\Gamma}^p$ with dimension d_p we find the matrices

$$\tilde{S}^p_j = \mu^p_j \cdot \tilde{1} \; . \tag{5.19}$$ 234r

The trace of the two sides of this equation and

$$\sum_{a\in\mathcal{C}_j} 1 = r_j \; ,$$

yields

$$\mu^p_j = \frac{r_j \chi^p_j}{d_p} \; . \tag{5.20}$$ 234rb

On the other hand, because of the definition of (5.18), it is

$$\tilde{S}^p_i \cdot \tilde{S}^p_j = \sum_{\substack{a\in\mathcal{C}_i \\ b\in\mathcal{C}_j}} \tilde{S}^p(a\cdot b) \overset{(2.7)}{=} \sum_{k=1}^{r} f_{ijk} \cdot \tilde{S}_k \; ,$$

where c_{ijk} are the multiplication coefficients introduced in Section 2.3.3. With Equations (5.19) and (5.20) we find

$$r_i \cdot r_j \cdot \chi^p_i \cdot \chi^p_j = d_p \sum_{k=1}^{r} f_{ijk} \cdot r_k \cdot \chi^p_k \; .$$

Next we carry out the sum over p on both sides and use Equation (5.17),

$$r_i \cdot r_j \sum_p \chi^p_i \cdot \chi^p_j = f_{ij1} \cdot r_1 \cdot g \; .$$

Recall that $r_1 = 1$ and with (2.8) we obtain

$$\sum_p \chi^p_i \cdot \chi^p_j = \frac{g}{r_j}\delta_{i,\bar{j}} \overset{j\to\bar{j}}{\Longrightarrow} \sum_p \chi^p_i \cdot \chi^p_{\bar{j}} = \frac{g}{r_j}\delta_{i,j} \; , \tag{5.21}$$ ki87

where we have used that a class and its inverse have the same number of elements, $r_{\bar{j}} = r_j$. To finish this part of the proof, we have to evaluate $\chi^p_{\bar{i}}$ in (5.21). With $a \in \mathcal{C}_j$ and $a^{-1} \in \mathcal{C}_{\bar{j}}$ we show in Exercise 7 that

$$\chi^p_{\bar{j}} = \left(\chi^p_j\right)^* \; .$$

As a result of this, we can write

$$\sum_p \chi^p_i \cdot \left(\chi^p_j\right)^* = \frac{g}{r_j}\delta_{i,j} \; ,$$

which proves the orthogonality theorem (5.10). Using this equation, we have also demonstrated that in the matrix of character vectors $(\vec{v}^1, \ldots, \vec{v}^{\bar{r}})$, not only are all columns orthogonal, but so are all rows. This implies that the rows must have a minimum dimension of r, meaning there are at least r distinct character vectors. Since we have already established in i) that there can be at most r distinct character vectors, we can now conclude that there are exactly r such vectors. This proves Theorem 1, which states that the number of classes corresponds to the number of irreducible representations.

These are g equations that connect the components of $\tilde{\alpha}^{(n)}$. Before we can analyze this relationship in more detail, we need the concept of a *product representation*, already introduced for practice purposes in Exercise 1 of Chapter 5.

9.2 Product Representations

⟨092sfre⟩ Let $\bar{\Gamma}^p, \Gamma^{p'}$ be irreducible representations of a group G. Then the product representation is defined as

$$\Gamma^{p\otimes p'}_{(ik),(jl)}(a) \equiv \Gamma^{p}_{i,j}(a)\cdot\Gamma^{p'}_{k,l}(a) : \qquad (9.6)$$ emjat

for all $a \in G$. The proof of $\bar{\Gamma}^{p\otimes p'}$ being a representation is simple,

$$\begin{aligned}\Gamma^{p\otimes p'}_{(ik),(jl)}(a\cdot b) &\overset{(9.6)}{=} \Gamma^{p}_{i,j}(a\cdot b)\cdot\Gamma^{p'}_{k,l}(a\cdot b)\\ &= \sum_{n,m}\Gamma^{p}_{i,n}(a)\cdot\Gamma^{p}_{n,j}(b)\cdot\Gamma^{p'}_{k,m}(a)\cdot\Gamma^{p'}_{m,l}(b)\\ &\overset{(9.6)}{=} \sum_{n,m}\Gamma^{p\otimes p'}_{(ik),(nm)}(a)\cdot\Gamma^{p\otimes p'}_{(nm),(jl)}(b)\ ,\end{aligned}$$

where, in the second step, we have used that $\bar{\Gamma}^p, \bar{\Gamma}^{p'}$ are representations.

Product representations can, of course, also be created with reducible representations. We then denote these as $\bar{\Gamma}\otimes\bar{\Gamma}'$. In this chapter, we will mainly consider such product representations.

Even for two irreducible representations, $\bar{\Gamma}^{p\otimes p'}$ is, in general, reducible. This already follows from the dimension, because if, for example, $\bar{\Gamma}^p$ has the maximum occurring dimension d_p of a group, then $\bar{\Gamma}^{p\otimes p}$ has the dimension d_p^2, so it must be reducible. Therefore, in general,

$$\bar{\Gamma}^{p\otimes p'} = \sum_{\tilde{p}} c(p,p'|\tilde{p})\cdot\bar{\Gamma}^{\tilde{p}}\ ,$$

with coefficients $c(p,p'|\tilde{p}) \in \mathbb{N}_0$.

The determination of the coefficients $c(p,p'|\tilde{p})$ succeeds as usual with Equation (5.23). For this we need the characters of the product representation, which can readily be calculated,

$$\chi^{p\otimes p'}(a) = \sum_{k,l}\Gamma^{p\otimes p'}_{(kl),(kl)}(a) \overset{(9.6)}{=} \sum_{k,l}\Gamma^{p}_{k,k}(a)\cdot\Gamma^{p'}_{l,l}(a) = \chi^{p}(a)\cdot\chi^{p'}(a)\ . \qquad (9.7)$$ bcswr

With (5.23) we then find

$$c(p,p'|\tilde{p}) = \frac{1}{g}\sum_i r_i\cdot\chi_i^{p\otimes p'}\cdot\left(\chi_i^{\tilde{p}}\right)^* \overset{(9.7)}{=} \frac{1}{g}\sum_i r_i\cdot\chi_i^{p}\cdot\chi_i^{p'}\cdot\left(\chi_i^{\tilde{p}}\right)^*\ . \qquad (9.8)$$ auyw4

With this equation and with the help of the character tables, we are now in the position to find all the coefficients of interest.

Example

As an example we consider the group D_3, and use its character Table 8.1 to find, for example, for the reduction of $\bar{\Gamma}^{E\otimes E}$:

$$\begin{aligned}c(E,E|A_1) &= \frac{1}{6}(\underbrace{1}_{=r_1}\cdot\underbrace{2\cdot 2}_{=\chi_1^{E\otimes E}}\cdot\underbrace{1}_{=\chi_1^{A_1}}+2\cdot(-1)\cdot(-1)\cdot 1+3\cdot 0\cdot 0\cdot 1) = 1\ ,\\ c(E,E|A_2) &= \frac{1}{6}(1\cdot 2\cdot 2\cdot 1+2\cdot(-1)\cdot(-1)\cdot 1+3\cdot 0\cdot 0\cdot 1) = 1\ ,\\ c(E,E|E) &= \frac{1}{6}(1\cdot 2\cdot 2\cdot 2+2\cdot(-1)\cdot(-1)\cdot(-1)+3\cdot 0\cdot 0\cdot(-1)) = 1\ .\end{aligned}$$

Hence, we obtain

$$\bar{\Gamma}^{p\otimes p'} = \bar{\Gamma}^{A_1} + \bar{\Gamma}^{A_2} + \bar{\Gamma}^{E} .$$

The results of reducing product representations from irreducible representations are summed up in tables known as *multiplication tables*. An example of such a table for the group D_3 can be seen in Table 9.1. It is worth noting that the use of the same names for both these tables and the group multiplication tables is unlikely to cause confusion in most cases. Multiplication tables are readily available on numerous websites.

The multiple product representations are defined in the same way

$$\bar{\Gamma} \equiv \bar{\Gamma}_1 \otimes \bar{\Gamma}_2 \otimes \cdots \otimes \bar{\Gamma}_n ,$$

with the representation matrices

$$\Gamma_{I,L}(a) \equiv \Gamma_{(i_1,\ldots,i_n),(l_1,\ldots,l_n)}(a) \equiv \Gamma^1_{i_1,l_1}(a) \cdot \Gamma^2_{i_2,l_2}(a) \cdots \Gamma^n_{i_n,l_n}(a) , \tag{9.9}$$ ooiq

where we have introduced the multiple indices

$$I \equiv (i_1, \ldots, i_n),\ L \equiv (l_1, \ldots, l_n) . \tag{9.10}$$ an76e

9.3 Independent Tensor Components

⟨yterdf43⟩ Our objective now is to identify all the interdependencies among the tensor components α_I and a set of independent components. Although in some specific cases, the components α_I can be selected independently, this is not generally the case. As we will see shortly, the independent parts of the tensor are typically expressed as linear combinations of the α_I components.

To begin our analysis, using the multiple indices notation (9.10), we first express Equation (9.5) as:

$$\alpha_I = \sum_L \Gamma_{L,I}(a) \cdot \alpha_L , \tag{9.11}$$ akj765

where[2]

$$\Gamma_{(l_1,\ldots,l_n),(i_1,\ldots,i_n)}(a) \equiv D_{l_1,i_1}(a) \cdots D_{l_n,i_n}(a) .$$

Up to this point, we have essentially argued with results from linear algebra. Now we want to bring in our knowledge of group theory. Let

$$\bar{\Gamma} = \sum_p n_p \cdot \bar{\Gamma}^p ,$$

be the reduction of $\bar{\Gamma}$ which is generated by some unitary matrix

$$S_{I,(p,m_p,\lambda_p)} \quad (m_p = 1, \ldots, n_p, \lambda_p = 1, \ldots, d_p) ,$$

[2] Recall that the three-dimensional rotation matrices of a point group are also a (generally reducible) representation (see Exercise 3 of Chapter 5).

D_3	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			$A_1 + A_2 + E$

Table 9.1: The multiplication table for the irreducible representations of the group D_3. Since the table is symmetrical (see Equation (9.8)) we have not specified all elements.
⟨lk67⟩

i.e.

$$\tilde{S}^\dagger \cdot \bar{\Gamma} \cdot \tilde{S} = \begin{pmatrix} \bar{\Gamma}^1 & & & & & & 0 \\ & \ddots & & & & & \\ & & \bar{\Gamma}^1 & & & & \\ & & & \ddots & & & \\ & & & & \bar{\Gamma}^r & & \\ & & & & & \ddots & \\ 0 & & & & & & \bar{\Gamma}^r \end{pmatrix} . \qquad (9.12)$$ shjq7

With the matrix $\tilde{S}$ we define the new tensor components

$$\beta_{(p,m_p,\lambda_p)} \equiv \sum_I S_{I,(p,m_p,\lambda_p)} \cdot \alpha_I ,$$

the inverse of which are given by

$$\alpha_I = \sum_p \sum_{m_p=1}^{n_p} \sum_{\lambda_p=1}^{d_p} S^*_{I,(p,m_p,\lambda_p)} \cdot \beta_{(p,m_p,\lambda_p)} . \qquad (9.13)$$ anht5

Our objective now is to examine which of the tensor components $\beta_{(p,m_p,\lambda_p)}$ can have non-zero values without violating Equation (9.11). To achieve this, we substitute Equation (9.13) into Equation (9.11),

$$\sum_{p,m_p,\lambda_p} S^*_{I,(p,m_p,\lambda_p)} \beta_{(p,m_p,\lambda_p)} = \sum_{L,p,m_p,\bar{\lambda}_p} \Gamma_{L,I}(a) \cdot S^*_{L,(p,m_p,\bar{\lambda}_p)} \cdot \beta_{(p,m_p,\bar{\lambda}_p)} .$$

We multiply this equation with $S_{I,(p',m_{p'},\lambda_{p'})}$ and sum over I. Then, with the unitarity of $\tilde{S}$ and Equation (9.12), it follows

$$\beta_{(p,m_p,\lambda_p)} = \sum_{\bar{\lambda}_p} \Gamma^p_{\lambda_p,\bar{\lambda}_p}(a) \cdot \beta_{(p,m_p,\bar{\lambda}_p)} . \qquad (9.14)$$ jduey656

If we represent the components in a vector with respect to λ_p and $\bar{\lambda}_p$, i.e.

$$\vec{\beta}_{p,m_p} \equiv (\beta_{p,m_p,1}, \ldots, \beta_{p,m_p,d_p})^T ,$$

we see that Equation (9.14) simply means that $\vec{\beta}_{p,m_p}$ is an eigenvector of every matrix $\tilde{\Gamma}^p(a)$ to the eigenvalue 1. We will now show that this implies that $\vec{\beta}_{p,m_p} = 0$ for all $p \neq 1$, where $p = 1$ corresponds to the trivial representation A_1, i.e. the one-dimensional representation for which $\Gamma^1(a) = 1$ for all a.

Proof:

i) If $d_p > 1$, the direction of $\vec{\beta}_{p,m_p} \neq \vec{0}$ would be a one-dimensional subspace that is invariant with respect to all $\tilde{\Gamma}^p(a)$. This leads to a contradiction with the statement that we formulated and proved at the beginning of Section 4.1.2.

ii) If $d_p = 1$ and $\beta_{p,m_p} \neq 0$ then it follows

$$\Gamma^p(a) \cdot \beta_{p,m_p} = \beta_{p,m_p} \quad \forall a .$$

which proves the statement.

With these findings we can now summarize the main results:

i) There are exactly n_1 independent tensor components β_{1,m_1}, i.e. as many as the number of occurrences of the representation $\bar{\Gamma}^1$ in the product representation (9.9).

ii) The tensor α_I can then be written as

$$\alpha_I = \sum_{m_1=1}^{n_1} S^*_{I,(1,m_1)} \cdot \beta_{(1,m_1)} \ . \tag{9.15}$$ ahhsy

where $\beta_{(1,m_1)}$ are the independent tensor components.

As usual, finding the number n_1 is easy in practice because one can use the standard Equation (5.23) for this purpose. The determination of the coefficients $S^*_{I,(1,m_1)}$ in (9.15) is a bit more difficult, but at least possible with elementary methods of linear algebra. The reason is that in Equation (9.12) we are only interested in the sector of the one representation, so we have to consider

$$\tilde{\mathcal{S}}^\dagger \cdot \tilde{\Gamma}(a) \cdot \tilde{\mathcal{S}} = \tilde{1}_{n_1 \times n_1} \ ,$$

instead of Equation (9.12). Here

$$\tilde{\mathcal{S}} = (\vec{s}_1, \ldots, \vec{s}_{n_1}) \ , \tag{9.16}$$ uyt

is a rectangular matrix and the the vectors $\vec{s}_{m_1}$ are exactly the coefficients $S^*_{I,(1,m_1)}$ in (9.15). When we multiply (9.16) with $\tilde{\mathcal{S}}$ from the left we obtain

$$\tilde{\Gamma}(a) \cdot \tilde{\mathcal{S}} = \tilde{\mathcal{S}} \ .$$

This implies that the vectors $\vec{s}_{m_1}$ are eigenvectors of all matrices $\tilde{\Gamma}(a)$ with an eigenvalue of 1. Although we cannot rule out the possibility that numerical mathematics may offer a better method, we provide a way to solve this problem numerically: First, we determine all eigenvectors of the matrices $\tilde{\Gamma}(a)$ that have an eigenvalue that is not equal to 1. Then, using the singular value decomposition,[3] we can find a basis $\vec{b}_i$ of the subspace spanned by these vectors. The vectors $\vec{s}_{m_1}$ that we need to find must be orthogonal to all $\vec{b}_i$. This leads to a homogeneous linear system of equations given by

$$(\vec{b}_1, \vec{b}_2, \ldots) \cdot \vec{s}_{m_1} = \vec{0} \ .$$

Once more, when it comes to numerically solving this problem, the singular value decomposition is likely the most effective tool.

Example

As an example, we consider a polarizability tensor $\tilde{\alpha}^{(2)}$ of rank 2 which we can analyze analytically. This leads to the 9-dimensional representation matrices

$$\Gamma_{(i,j),(k,l)}(a) = D_{i,k}(a) \cdot D_{j,l}(a) \ . \tag{9.17}$$ uh16a

With these, we obtain for the characters

$$\chi(a) = \underbrace{\sum_i D_{i,i}(a)}_{\equiv \bar{\chi}(a)} \cdot \sum_j D_{j,j}(a) = \bar{\chi}(a)^2 = \bar{\chi}_i^2 \ .$$

[3] William H. Press et al. Numerical Recipes in C: the Art of Scientific Computing. Cambridge [Cambridgeshire]; New York: Cambridge University Press, 1992.

i) $a, b \in G_0$: it is obviously $\tilde{D}'(a \cdot b) = \tilde{D}'(a) \cdot \tilde{D}'(b)$ $\surd$

ii) $a \in G_0$, $b \in L_0$:

$$\tilde{D}'(\underbrace{a \cdot b}_{\in L_0}) = -\tilde{D}(a \cdot b) = \tilde{D}(a) \cdot (-\tilde{D}(b)) = \tilde{D}'(a) \cdot \tilde{D}'(b) \ \surd$$

iii) $a, b \in L_0$:

$$\tilde{D}'(\underbrace{a \cdot b}_{\in G_0}) = \tilde{D}(a \cdot b) = (-\tilde{D}(a)) \cdot (-\tilde{D}(b)) = \tilde{D}'(a) \cdot \tilde{D}'(b) \ \surd$$

The same then applies to product representations built with the matrices $\tilde{D}'(a)$ $\surd$.

9.4 Tensor Operators

⟨uq756⟩ 9.4.1 Definition of Tensor Operators

Let us consider a quantum mechanical system with a symmetry group G whose elements of unitary operators are denoted as $\hat{U}_a$. A set of operators $\hat{T}_{i_1,\ldots,i_n}$ is then referred to as *tensor operators of rank* n if they transform according to the following equation,

$$\hat{U}_a \cdot \hat{T}_{i_1,\ldots,i_n} \cdot \hat{U}_a^\dagger = \sum_{l_1,\ldots,l_n} [\Gamma_{l_1,i_1}(a) \cdots \Gamma_{l_n,i_n}(a)] \cdot \hat{T}_{l_1,\ldots,l_n} \ , \tag{9.20}$$ aj713

where $\bar{\Gamma}$ is a (usually reducible) representation of G. As examples of such operators, we can consider those that act on the Hilbert space of square-integrable functions.

i) *Vector operators* are tensor operators of rank $n = 1$. An example are the three components $\hat{x}_i$ of the position vector operator $\hat{\vec{r}}$. They transform like (see Exercise 1)

$$\hat{U}_{\tilde{D}} \cdot \hat{\vec{r}} \cdot \hat{U}_{\tilde{D}}^\dagger = \tilde{D} \cdot \hat{\vec{r}} \ , \tag{9.21}$$ u6e7s

or expressed by the components

$$\hat{U}_{\tilde{D}} \cdot \hat{x}_i \cdot \hat{U}_{\tilde{D}}^\dagger = \sum_j D_{i,j} \cdot \hat{x}_j \ . \tag{9.22}$$ jjhdt

This equation indeed corresponds to (9.20), since $D_{i,j} = (\tilde{D}^{-1})^*_{j,i}$ and the set of matrices $(\tilde{D}^{-1})^*$ is also a representation of a point group. Obviously, the momentum operator $\hat{\vec{p}}$ of a particle is also a vector operator.

ii) The operators

$$\hat{T}_{i,j} \equiv \hat{x}_i \cdot \hat{x}_j \ ,$$

built with the components of the position vector operator form a tensor operator of rank 2. This is shown in Exercise 6.

iii) One can also consider the case $n = 0$ (*scalar operators*) which transform like

$$\hat{U}_{\tilde{D}} \cdot \hat{T}_0 \cdot \hat{U}_{\tilde{D}}^\dagger = \hat{T}_0 (= \underbrace{1}_{\bar{\Gamma}(\tilde{D})=1 \ \forall \tilde{D}} \hat{T}_0) \ ,$$

Chapter 10

Matrix Elements of Tensor Operators: The Wigner-Eckart Theorem

⟨shjye⟩ In this chapter, we focus on the Wigner-Eckart theorem, which allows us to calculate matrix elements of irreducible tensor components. In Section 10.1, we first recall a common variant of this theorem that is usually covered in quantum mechanics courses. In this context, we also introduce the concept of Clebsch-Gordan coefficients. In Section 10.2, we explore the significance of matrix elements in perturbation theory. The coupling coefficients, which are crucial in formulating the Wigner-Eckart theorem, are discussed in Section 10.3. Finally, in Section 10.4, we formulate and proof the Wigner-Eckart theorem with group-theoretical means.

10.1 Clebsch-Gordan Coefficients and the Wigner-Eckart Theorem for Angular Momenta

⟨ak1854⟩ 10.1.1 Clebsch-Gordan Coefficients

As is usually shown in introductory lectures on quantum mechanics, the Hilbert space of a system of two angular momenta $\hat{\vec{J}}_1$, $\hat{\vec{J}}_2$ can be spanned with the base

$$|j_1, m_1; j_2, m_2\rangle \equiv |j_1, m_1\rangle |j_2, m_2\rangle \tag{10.1}$$ iia764

where $|j_i, m_i\rangle$ $(m_i = -l_i, \ldots, l_i)$ is the basis of the Hilbert-space of the angular momentum $\hat{\vec{J}}_i$. The basis states (10.1) have the well-known properties ($\hbar = 1$, $i = 1, 2$)

$$\begin{aligned}
\hat{\vec{J}}_i^2 |j_1, m_1; j_2, m_2\rangle &= j_i(j_i + 1)|j_1, m_1; j_2, m_2\rangle \ , \\
\hat{J}_{i,z} |j_1, m_1; j_2, m_2\rangle &= m_i |j_1, m_1; j_2, m_2\rangle \quad (m_i = -j_i, \ldots, j_i).
\end{aligned}$$

An alternative basis consists of eigenstates of $\hat{\vec{J}}^2$, $\hat{J}_z$ and $\hat{\vec{J}}_i^2$ where

$$\hat{\vec{J}} \equiv \hat{\vec{J}}_1 + \hat{\vec{J}}_2 \ .$$

The eigenvalue equations of $\hat{\vec{J}}^2$ and $\hat{J}_z$ are

$$\begin{aligned}
\hat{\vec{J}}^2 |j, m; j_1, j_2\rangle &= j(j + 1)|j, m; j_1, j_2\rangle \ , \ \ j = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2 \ , \\
\hat{J}_z |j, m; j_1, j_2\rangle &= m|j, m; j_1, j_2\rangle \ \ m = -j, \ldots, j \ .
\end{aligned}$$

Apparently, the two bases can be expressed by each other,

$$|j,m;j_1,j_2\rangle = \sum_{m_1,m_2} \left(\begin{array}{cc|c} j_1 & j_2 & j \\ m_1 & m_2 & m \end{array} \right) |j_1,m_1;j_2,m_2\rangle \ ,$$

where the coefficients in this equation are denoted as *Clebsch-Gordan coefficients*. How to calculate these coefficients is shown in most books on quantum mechanics. They play a crucial role in the Wigner-Eckart theorem, which we formulate next.

10.1.2 The Wigner-Eckart Theorem for Angular Momenta

Some readers may have already learned about the Wigner-Eckart theorem for angular momenta in their introductory lecture on quantum mechanics. We will briefly review this theorem before generalizing it for general symmetry groups.

Analogous to Equation (9.26), we define a set of $2j+1$ operators $\hat{T}_{j,m}$ $(m = -j,\ldots,j)$ that behave like

$$\tilde{U}_{\tilde{D}} \cdot \hat{T}_{j,m} \cdot \tilde{U}^{\dagger}_{\tilde{D}} = \sum_{m'=-j}^{j} R^{j}_{m,m'}(\tilde{D}) \cdot \hat{T}_{j,m'}$$

under rotations $\tilde{D} \in O(3)$ as *irreducible spherical tensor operators of rank* j. Here the rotation matrix $R^{j}_{m,m'}(\tilde{D})$ is given by the matrix elements

$$R^{j}_{m,m'}(\tilde{D}) \equiv \langle j,m|\tilde{U}^{\dagger}_{\tilde{D}}|j,m'\rangle$$

of the rotation operator $\tilde{U}^{\dagger}_{\tilde{D}}$ in the subspace j. For example, a tensor operator of rank $j=1$ consists of three components which results from an arbitrary vector operator $\hat{\vec{V}}$, if we define

$$\begin{aligned} \hat{T}_{1,\pm 1} &\equiv \mp\frac{1}{\sqrt{2}}(\hat{V}_x \pm \hat{V}_y) \ , \\ \hat{T}_{1,0} &\equiv \hat{V}_z \ . \end{aligned}$$

The Wigner-Eckart theorem then states that for any matrix element of states $|j_1,m_1\rangle$, $|j_2,m_2\rangle$ it holds

$$\langle j_1,m_1|\hat{T}_{j,m}|j_2,m_2\rangle = \left(\begin{array}{cc|c} j_1 & j_2 & j \\ m_1 & m_2 & m \end{array} \right) \Omega(j,j_1,j_2) \ , \qquad (10.2)$$ fhjjrt

with quantities $\Omega(j,j_1,j_2)$, for which it is crucial that they do not depend on m_1,m_2,m. The dependency on the latter quantum numbers is determined entirely by the Clebsch-Gordan coefficients. The calculation or measurement of the matrix elements (10.2) is therefore reduced to determining the usually much smaller number of quantities $\Omega(j,j_1,j_2)$.

10.2 Matrix Elements in the Time-Dependent Perturbation Theory

⟨ak1854b⟩ As discussed in Chapter 8, the evaluation of matrix elements is important in time-independent perturbation theory. However, the evaluation of matrix elements with tensor operators is even more crucial in time-dependent perturbation theory. In this approximation, one typically deals with a Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_0 + f(t) \cdot \hat{V} \ .$$

Appendix A

The Schoenflies and the International Notation

⟨app1⟩ There are two established ways of naming point groups, the *Schoenflies* and the *international notation*. The Schoenflies notation is used more often if one is only interested in the point groups. In contrast, the international one is mainly to denote the rotational part of space groups. We will give a brief introduction to both notations in this appendix.

A.1 The Schoenflies notation

?⟨app1a⟩? In the Schoenflies notation, the proper point groups are named in the same way as they were introduced in Section 3.2. Most of the names of the improper point groups are derived from those of the proper ones by specifying which additional improper symmetry operations exist in the group. Historically, the notation of the groups argued with the existing mirror planes and did not use the inversion. We go a slightly different way here to motivate the notation:

i) The groups $C_i, C_{2h}, S_6, C_{4h}, D_{2h}, D_{3d}, C_{6h}, D_{4h}, D_{6h}, T_h, O_h$:
These groups are constructed by adding the inversion I to the respective 11 proper point groups G_0 in (3.7), $G = G_0 \times (E, I)$. For the proper point groups $G_0 = \{C_1, C_3\}$ the notations C_i, S_6 are used instead of C_{1h}, C_{3h}. Remember that all these groups also contain some mirror planes, since these correspond to a product of a two-fold rotation and the inversion (see Section 3.1).

ii) The groups C_s, C_{3h}, D_{3h}:
These groups are constructed by adding a mirror plane σ_h perpendicular to the main symmetry axis δ_n to the respective proper point groups C_1, C_3, D_3. In case of D_3 the two-fold axes, perpendicular to δ_n, must obviously lie in σ_h.

iii) The groups C_{nv} $(n = 2, 3, 4, 6)$:
These groups are constructed by adding n mirror planes to C_n $(n = 2, 3, 4, 6)$ that all contain the axis of symmetry and have the same angle relative to each other.

iv) The groups S_4, D_{2d}, T_d $(n = 2, 3, 4, 6)$:
These groups are constructed by replacing the two-fold symmetry axis in C_2, D_2, T by a four-fold *rotary inversion* axis $\sigma_4 \equiv I \cdot \delta_4$. Since $(\sigma_4)^2 = \delta_2$, the corresponding proper groups are subgroups in all three cases. Note that T_d is the symmetry group of a tetrahedron.

$\bar{n}$	elements	order $g(\bar{n})$
$\bar{1}$	$E \quad I$	2
$\bar{2} \equiv m$	$E \quad \sigma$	2
$\bar{3}$	$E \quad \sigma_6 \quad \delta_3^{-1} \quad I \quad \delta_3 \quad \sigma_6^{-1}$	6
$\bar{4}$	$E \quad \sigma_4 \quad \delta_2 \quad \sigma_4^{-1}$	4
$\bar{6}$	$E \quad \sigma_3 \quad \delta_3 \quad \sigma \quad \delta_3^{-1} \quad \delta_3^{-1}$	6

Table A.1: Elements of a rotary inversion axes $\bar{n}$

$\bar{n}$	elements	order $g\left(\frac{n}{m}\right)$
$\frac{2}{m}$	$E \quad \sigma \quad I \quad \delta_2$	4
$\frac{4}{m}$	$E \quad \sigma_4 \quad \delta_2 \quad \sigma_4^{-1} \quad I \quad \delta_4 \quad \sigma \quad \delta_4^{-1}$	8
$\frac{6}{m}$	$E \quad \sigma_3 \quad \delta_3 \quad \sigma \quad \delta_3^{-1} \quad \delta_3^{-1} \quad I \quad \delta_6 \quad \sigma_6 \quad \delta_2 \quad \sigma_6^{-1} \quad \delta_6^{-1}$	12

Table A.2: Elements of a rotary inversion axes $\frac{n}{m}$ for even n

A.2 The International notation

⟨app1b⟩ The international notation considers the three possible types of rotational symmetry axes:

i) proper n-fold rotation axes δ_n are denoted as $n = 2, 3, 4, 6$.

ii) n-fold rotary inversion axes $I \cdot \delta_n$ are denoted as $\bar{n}$ with $n = 1, 2, 3, 4, 6$. Then, an axis $\bar{n}$ contains the symmetry elements shown in Table A.1. In that table we use the common abbreviations

$$\sigma_2 \equiv \sigma \equiv I \cdot \delta_2 \ , \ \sigma_6 \equiv I \cdot \delta_3 \ , \ \sigma_4 \equiv I \cdot \delta_4 \ , \ \sigma_3 \equiv I \cdot \delta_6 \ .$$

Since a rotary inversion axes $\bar{2}$ is equivalent to a mirror plane, one often writes 'm' instead of '$\bar{2}$' .

iii) If n is odd, $\bar{n}$ necessarily contains I, because

$$(I \cdot \delta_n)^n = \underbrace{I^n}_{I} \cdot \underbrace{\delta_n^n}_{E} = I$$

Therefore, the definition of the third kind of axes of rotation only makes sense for even n:

$$\frac{n}{m} \equiv \bar{n} \cup I$$

The elements of an axis $\frac{n}{m}$ are shown in Table A.2.

We can now formulate the rules of the international notation.

i) Identify all occurring axes of the form $n, \bar{n}, \frac{n}{m}$.

ii) Equivalent axes are represented by a common symbol. Equivalence here means that the axes can be mapped onto one another by a symmetry operation. An exception is the group $D_2 = 222$, where all three axes occur since otherwise the group would not be distinguishable from $C_2 = 2$.

iii) The symbol of the point group is then simply the list of the occuring symbols $n, \bar{n}, \frac{n}{m}$. sorted according to the order of the axes. Again there are expections, like $T = 23$, which has to be distinguished from $D_3 = 32$.

Appendix B

Solutions to the Exercises

⟨solutions⟩

Chapter 1

1. It is sufficient to show that

$$\langle\vec{r}|\hat{T}_{\tilde{D}^{-1}}\cdot\hat{T}_{\tilde{D}}|\vec{r}'\rangle=\delta(\vec{r}-\vec{r}')\ , \tag{B.1}$$ q66atr

for all basis states $|\vec{r}\rangle$, $|\vec{r}'\rangle$. When we insert a one-operator $\hat{1}$ built with these states, we find

$$\begin{aligned}\langle\vec{r}|\hat{T}_{\tilde{D}^{-1}}\cdot\hat{T}_{\tilde{D}}|\vec{r}'\rangle &= \int \mathrm{d}^3r''\langle\vec{r}|\hat{T}_{\tilde{D}^{-1}}|\vec{r}''\rangle\langle\vec{r}''|\hat{T}_{\tilde{D}}|\vec{r}'\rangle\\ &= \int \mathrm{d}^3r''\langle\tilde{D}^{-1}\cdot\vec{r}|\vec{r}''\rangle\langle\tilde{D}\cdot\vec{r}''|\vec{r}'\rangle\ .\end{aligned} \tag{B.2}$$ 881rwe

Since

$$\langle\tilde{D}^{-1}\cdot\vec{r}|\vec{r}''\rangle=\langle\vec{r}|\tilde{D}\cdot\vec{r}''\rangle=\delta(\vec{r}-\tilde{D}\cdot\vec{r}'')$$

and

$$\langle\tilde{D}\cdot\vec{r}''|\vec{r}'\rangle=\delta(\vec{r}'-\tilde{D}\cdot\vec{r}'')$$

Equation (B.1) follows from (B.2).

2. a) With the definition of the momentum operator $\hat{\vec{p}}=-\mathrm{i}\hbar\vec{\nabla}$, it follows

$$\hat{T}_{\vec{a}}\cdot\Psi(\vec{r})=\sum_{j=1}^{\infty}\frac{1}{j!}(\vec{a}\cdot\vec{\nabla})^j\Psi(\vec{r})$$

which is just the Taylor-expansion of $\Psi(\vec{r}+\vec{a})$.

b) In spherical coordinates it is $\hat{L}_z=\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\varphi}$. Thus, we find

$$\hat{T}_\alpha\cdot\Psi(r,\theta,\varphi)=\sum_{j=1}^{\infty}\frac{1}{j!}\left(\frac{\partial}{\partial\varphi}\right)^j\Psi(r,\theta,\varphi)=\Psi(r,\theta,\varphi+\alpha)\ .\surd$$

Since the z-direction is not distinguished from all other, for any other direction $\vec{e}$ ($|\vec{e}|=1$) of the rotation it must be

$$\hat{T}_{\alpha,\vec{e}}=\exp\left(\frac{\mathrm{i}}{\hbar}\alpha\left(\vec{e}\cdot\hat{\vec{L}}\right)\right)=\exp\left(\vec{\alpha}\cdot\hat{\vec{L}}\right)\equiv\hat{T}_{\vec{\alpha}}$$

with a vector $\vec{\alpha}\equiv\alpha\cdot\vec{e}$.

3. We follow the idea for a proof proposed in the exercise:

   i) Using well-known properties of determinants we can derive:

$$\begin{aligned}|\tilde{1} - \tilde{D}| &= \underbrace{|\tilde{D}|}_{=1}|\tilde{1} - \tilde{D}| = |\tilde{D}^T||\tilde{1} - \tilde{D}| = |\tilde{D}^T - \tilde{1}| = |\tilde{D} - \tilde{1}| \\ &= -|\tilde{1} - \tilde{D}| \ .\end{aligned}$$

   Therefore, it is $|\tilde{1} - \tilde{D}| = 0$, which means that $\lambda = 1$ is an eigenvalue of $\tilde{D}$.

   ii) In a complex vector space, $\tilde{D}$ has 3 complex eigenvalues λ_i and there is a unitary matrix $\tilde{U}$ such that

$$\tilde{U} \cdot \tilde{D} \cdot \tilde{U}^\dagger = \tilde{D}^{\mathrm{d}} \equiv \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} .$$

   With

$$\tilde{D}^{\mathrm{d}} \cdot (\tilde{D}^{\mathrm{d}})^\dagger = \tilde{U} \cdot \tilde{D} \cdot \tilde{U}^\dagger \cdot \tilde{U} \cdot \tilde{D}^\dagger \cdot \tilde{U}^\dagger = \tilde{U} \cdot \tilde{D} \cdot \tilde{D}^\dagger \cdot \tilde{U}^\dagger = \tilde{U} \cdot \tilde{U}^\dagger = \tilde{1} \ ,$$

   we can conclude that

$$|\lambda_i|^2 = 1 \quad \Rightarrow \quad \lambda_i = e^{\mathrm{i}\varphi_{\mathrm{i}}} \ ,$$

   with $\varphi_i \in \mathbb{R}$. Since one of these eigenvalues is 1 (e.g. $\varphi_3 = 0$) and $|\tilde{D}| = |\tilde{D}^{\mathrm{d}}| = 1$, it must be $\varphi_1 = -\varphi_2 \equiv \varphi$.

   iii) For $\varphi \neq 0$, the three eigenvectors $\vec{v}_i$ are orthogonal, because[1]

$$\vec{v}_i^\dagger \cdot \tilde{D} \cdot \vec{v}_j = e^{\mathrm{i}\varphi_{\mathrm{i}}} \vec{v}_i^\dagger \cdot \vec{v}_j = e^{\mathrm{i}\varphi_{\mathrm{j}}} \vec{v}_i^\dagger \cdot \vec{v}_j \quad \Rightarrow \quad \vec{v}_i^\dagger \cdot \vec{v}_j = \delta_{i,j} \ .$$

   If we split the two vectors $\vec{v}_1$, $\vec{v}_2$ into their real and imaginary parts

$$\vec{v}_{1,2} = \frac{1}{\sqrt{2}}(\vec{v}_{\mathrm{R}} \pm \mathrm{i}\vec{\mathrm{v}}_{\mathrm{I}}) \ ,$$

   the real vectors $\vec{v}_{\mathrm{R}}$, $\vec{v}_{\mathrm{I}}$ are also orthogonal. We can then use the inverse

$$\begin{aligned}\vec{v}_{\mathrm{R}} &= \frac{1}{\sqrt{2}}(\vec{v}_1 + \vec{v}_2) \ , \\ \vec{v}_{\mathrm{I}} &= \frac{1}{\mathrm{i}\sqrt{2}}(\vec{v}_1 - \vec{v}_2)\end{aligned}$$

   to calculate the 4 matrix elements $\vec{v}_{\mathrm{R,I}} \cdot \tilde{D} \cdot \vec{v}_{\mathrm{R,I}}$. This results in the following matrix in the basis of the (real) vectors $\vec{v}_{\mathrm{R}}, \vec{v}_{\mathrm{I}}, \vec{v}_3$

$$\tilde{D}' = \begin{pmatrix} \cos(\varphi) & \sin(\varphi) & 0 \\ -\sin(\varphi) & \cos(\varphi) & 0 \\ 0 & 0 & 1 \end{pmatrix} . \checkmark$$

4. a) The symmetry transformations are

      i) Three axes of rotation $\vec{e}_x, \vec{e}_y, \vec{e}_z$ with rotation angles of π.

      ii) The inversion at the origin.

[1] Remember that $\hat{D}^T \vec{v}_i = e^{-\mathrm{i}\varphi} \vec{v}_i$.

iii) Three mirror planes, in each of which there are two axes of rotation.

We refer to this symmetry group in Chapter 3 as D_{2h}.

b) The symmetry transformations are

i) An axis of rotation $\vec{e}_z$ with a rotation angle of π.

ii) The inversion at the origin.

iii) The mirror plane perpendicular to the axis of rotation.

iv) The two rotation axes $y = x$ and $y = -x$ with a rotation angle of π. They induce the transformation

$$x \to y \text{ and } y \to x \ ,$$

and

$$x \to -y \text{ and } y \to -x \ .$$

v) Two mirror planes parallel to $\vec{e}_z$ in which the rotation axes iv) lie.

A comparison with a) shows that this is exactly the same group D_{2h}.

Chapter 2

1. a) Suppose that there are two elements $E_1 \neq E_2$ with $E_1 \cdot a = a$ and $E_2 \cdot a = a$ for all $a \in G$. Multiplying

$$E_1 \cdot a = E_2 \cdot a$$

from the right with a^{-1} yields $E_1 = E_2$. $\surd$

b) The proof is the same as in a) replacing E_i by a_i^{-1}.

c) Let us assume that for every $a \in G$ there is a left inverse element a_{L}^{-1} with

$$a_{\mathrm{L}}^{-1} \cdot a = E \ .$$

If we multiply this equation from the left with a it follows

$$a \cdot a_{\mathrm{L}}^{-1} \cdot a = a \quad \Rightarrow \quad a \cdot a_{\mathrm{L}}^{-1} = E \quad \Rightarrow \quad a_{\mathrm{R}}^{-1} = a_{\mathrm{L}}^{-1} \ . \surd$$

2. With Table 2.5 we find for the class multiplications ($\mathcal{C}_1 \cdot \mathcal{C}_i = \mathcal{C}_i$ obviously holds)

$$\begin{aligned} \mathcal{C}_2 \cdot \mathcal{C}_3 &= \{\delta_3 \cdot \delta_{21}, \delta_3 \cdot \delta_{22}, \delta_3 \cdot \delta_{23}, \delta_3^2 \cdot \delta_{21}, \delta_3^2 \cdot \delta_{22}, \delta_3^2 \cdot \delta_{23}\} \\ &= \{\delta_{23}, \delta_{21}, \delta_{22}, \delta_{22}, \delta_{23}, \delta_{21}\} = 2\mathcal{C}_3 \ , \surd \\ \mathcal{C}_3 \cdot \mathcal{C}_3 &= \{\delta_{21} \cdot \delta_{21}, \delta_{21} \cdot \delta_{22}, \delta_{21} \cdot \delta_{23}, \delta_{22} \cdot \delta_{21}, \delta_{22} \cdot \delta_{22}, \delta_{22} \cdot \delta_{23}, \\ &\qquad \delta_{23} \cdot \delta_{21}, \delta_{23} \cdot \delta_{22}, \delta_{23} \cdot \delta_{23}\} \\ &= \{E, \delta_3, \delta_3^2, \delta_3^2, E, \delta_3, \delta_3, \delta_3^2, E\} = 3\mathcal{C}_1 \cdot \mathcal{C}_2 \ . \surd \end{aligned}$$

3. If $f(a) = a^{-1}$ satisfies (2.15), we have

$$\underbrace{(a^{-1} \cdot b^{-1})^{-1}}_{=b \cdot a} = \underbrace{(a^{-1})^{-1} \cdot (b^{-1})^{-1}}_{a \cdot b} \ . \surd$$

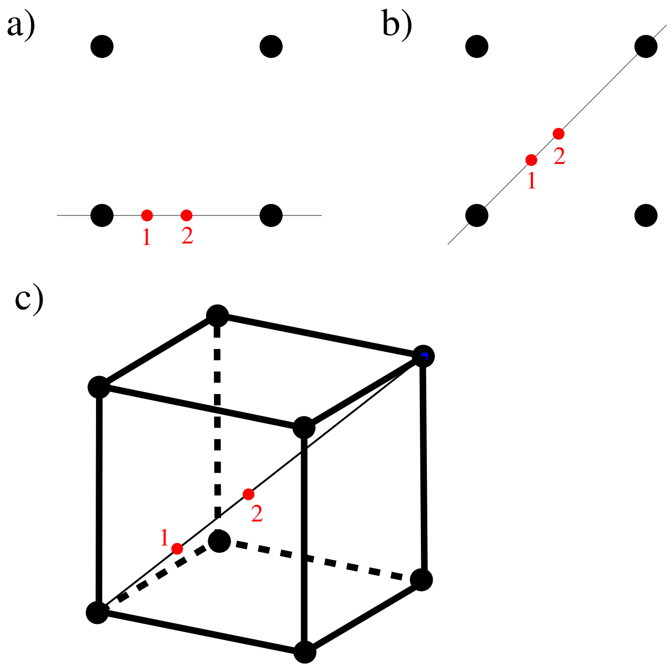

Figure B.3: The position of an additional atom in a cubic lattice.

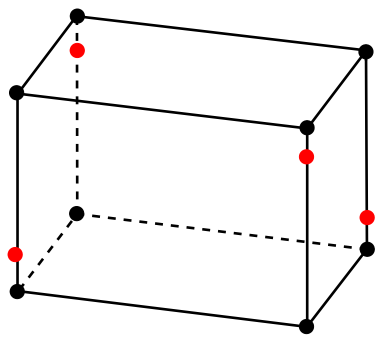

Figure B.4: An artificial molecule with the symmetry group D_2.

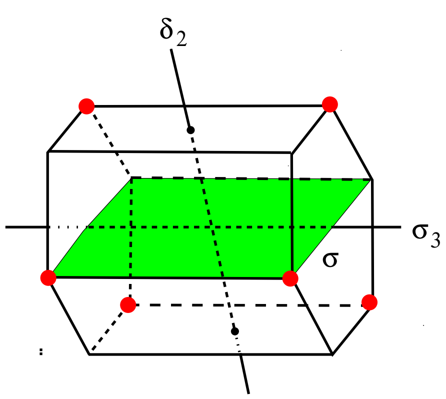

Figure B.5: An artificial molecule with the symmetry group D_{3h}. Shown are the 6-fold rotation inversion axis (σ_3) and one of the three 2-fold rotation axes (σ_2) and one of the mirror planes σ.

ii) The group D_{3h} contains a 6-fold rotation inversion axis, as well as three 2-fold axes of rotation and mirror planes. The inversion is no symmetry operation. This leads to a similar situation as in Figure B.2, except that the two faces (left and right) must be chosen as regular hexagon (see the six (red) atoms in Figure B.5).

6. The only symmetry that exists in any 2-dimensional system is the mirror plane. Together with the identity element, this leads to the group C_s.

7. It becomes D_{3d}.

8. Given that two point groups are equivalent, there is, then, a matrix $\tilde{S}$ with

$$\tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} = \tilde{D}'_i \ ,$$

for all matrices $\tilde{D}_i$, $\tilde{D}'_i$ of the two groups. This equation then obviously also defines the isomorphism $\tilde{D}_i \leftrightarrow \tilde{D}'_i$, because

$$\tilde{D}'_l = \tilde{D}'_i \cdot \tilde{D}'_j = (\tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S}) \cdot (\tilde{S}^{-1} \cdot \tilde{D}_j \cdot \tilde{S}) = \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{D}_j \cdot \tilde{S} = \tilde{S}^{-1} \cdot \tilde{D}_l \cdot \tilde{S} \ . \checkmark$$

9. Suppose that $C_2 \times C_4$ is isomorphic to C_8. Then, there must be a generating element $(a;b) \in C_2 \times C_4$ with $a \in C_2$ and $b \in C_4$ and

$$(a;b)^l = E \ . \tag{B.3}$$

for (and only for) $l = 8$. a and b can be written as $a = a_{\mathrm{g}}^m$, $b = b_{\mathrm{g}}^n$ with generating elements a_{g}, b_{g} and some natural numbers m, n. Then, it follows

$$(a;b)^4 = (a_{\mathrm{g}}^m; b_{\mathrm{g}}^n)^4 = (a_{\mathrm{g}}^{4m}; b_{\mathrm{g}}^{4n}) = (E;E) = E$$

in contradiction to Equation (B.3) , i.e. $C_2 \times C_4$ is not isomorphic to C_8.

Chapter 5

1. a) If $a_i \sim a'_i$ and $b_j \sim b'_j$ there must be $a \in G_1$ and $b \in G_2$ such that

$$a_i = a^{-1} \cdot a'_i \cdot a \ \ \vee \ \ b_j = b^{-1} \cdot b'_j \cdot b \ \ \Rightarrow \ \ (a_i; b_j) = (a;b)^{-1} \cdot (a'_i; b'_j) \cdot (a;b)$$

and therefore $(a_i; b_j) \sim (a'_i; b'_j)$. Since the argument also works in the opposite direction, the assertion holds. Hence, for every pair of classes $\mathcal{C}_k \in G_1$, $\mathcal{C}_l \in G_2$ there exists a class $\mathcal{C}_{[k,l]} \in G_1 \times G_2$ that consists of all pairs (a_i, b_j) with $a_i \in \mathcal{C}_k$, $b_j \in \mathcal{C}_l$. The number of elements in $\mathcal{C}_{[k,l]}$ is $r_{[k,l]} = r_k \cdot r_l$.

b) The proof of the representation property is straightforward:

$$\begin{aligned}
\Gamma^{1\otimes 2}_{(i,j),(k,l)}((a;b)\cdot(a';b')) &= \Gamma^{1\otimes 2}_{(i,j),(k,l)}((a\cdot a'; b\cdot b')) \\
&= \Gamma^1_{i,k}(a\cdot a') \cdot \Gamma^2_{j,l}(b\cdot b') \\
&= \sum_{p,q} \Gamma^1_{i,p}(a)\cdot\Gamma^1_{p,j}(a')\cdot\Gamma^2_{j,q}(b)\cdot\Gamma^2_{q,l}(b') \\
&= \sum_{p,q} \Gamma^{1\otimes 2}_{(i,j),(p,q)}((a;b))\cdot\Gamma^{1\otimes 2}_{(p,q),(k,l)}((a';b')) \ . \checkmark
\end{aligned}$$

c) To show the irreducibility, we use Equation (5.24). We know the number of elements $r_{[i,j]}$ from a). Then, we need the character (with some elements $a_i \in \mathcal{C}_i$, $b_j \in \mathcal{C}_j$)

$$\chi_{[i,j]} = \sum_{k,l} \Gamma^{1\otimes 2}_{(k,l),(k,l)}((a_i;b_j)) = \sum_{k,l} \Gamma^1_{k,k}(a_i) \cdot \Gamma^2_{l,l}(b_j) = \chi^1_i \cdot \chi^2_j \ .$$

Hence, we obtain

$$\sum_{[i,j]} = r_{[i,j]}|\chi_{[i,j]}|^2 = \left(\sum_i r_i|\chi^1_i|\right)\left(\sum_j r_j|\chi^2_j|\right) = g_1 \cdot g_2 = g \ . \checkmark$$

2. We need the irreducible representations of the two groups D_3 and C_2 given in Tables 4.1 and 6.1. The product matrices then lead to the irreducible representations of D_{3d}, which we give in Table 2.16.

	E	δ_3	δ_3^2	δ_{21}	δ_{22}	δ_{23}	I	$(I\delta_3)$	$(I\delta_3^2)$	$(I\delta_{21})$	$I\delta_{22})$	$I\delta_{23})$
$\Gamma^{A\otimes A}$	1	1	1	1	1	1	1	1	1	1	1	1
$\Gamma^{B\otimes A}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
$\Gamma^{E\otimes A}$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$
$\Gamma^{A\otimes B}$	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
$\Gamma^{B\otimes B}$	-1	-1	-1	1	1	1	-1	-1	-1	1	1	1
$\Gamma^{E\otimes B}$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$	$-\tilde{D}_1$	$-\tilde{D}_2$	$-\tilde{D}_3$	$-\tilde{D}_4$	$-\tilde{D}_5$	$-\tilde{D}_6$

Table B.5: Irreducible representations of the group D_{3d}. The matrices $\tilde{D}_i$ are defined in Equation (2.16).

3. As always in this context we use Equation (5.23). The characters χ^p_i are given in Table 5.1, those of the three-dimensional orthogonal matrices can be calculated with Equation (3.5). For the group D_2 one finds

$$\chi(E) = 3, \chi(\delta_{2,i}) = -1 \ .$$

Thus, it is

$$\begin{aligned} n_A &= \frac{1}{4}(1\cdot 1\cdot 3 + 1\cdot 1\cdot(-1) + 1\cdot 1\cdot(-1) + 1\cdot 1\cdot(-1)) \ , \\ &= \frac{1}{4}(3-1-1-1) = 0 \ , \\ n_{B_1} &= \frac{1}{4}(3+1+1-1) = 1 = n_{B_2} = n_{B_3} \ , \end{aligned}$$

and

$$\Gamma = \Gamma^{B_1} \oplus \Gamma^{B_2} \oplus \Gamma^{B_3} \ .$$

For the group D_3 the relevant characters are

$$\chi(E) = 3, \chi(\delta_3) = \chi(\delta_3^2) = 0, \chi(\delta_{2,i}) = -1 \ .$$

Hence,

$$\begin{aligned} n_{A_1} &= \frac{1}{6}(1\cdot 1\cdot 3 + 2\cdot 0\cdot 1 + 3\cdot 1\cdot(-1)) = 0 \ , \\ n_{A_2} &= \frac{1}{6}(3+0+3) = 1 \ , \\ n_E &= \frac{1}{6}(6+0+0) = 1 \ , \end{aligned}$$

5. We take the sum over $i = j$ and $l = k$ in (5.2),

$$\sum_{a\in G} \chi(a) \cdot \chi(a)^* = \sum_{a\in G} |\chi(a)|^2 = \frac{g}{d} \sum_{i,l} \delta_{i,j}\delta_{l,k}\delta_{i,l}\delta_{j,k} = \frac{g}{d} \underbrace{\sum_{i} 1}_{=d} = g \; .$$

Since the characters $\chi(a)$ are identical in a class, we obtain Equation (5.24) and thus $\bar{\Gamma}$ is irreducible.

6. In order to evaluate Equation (5.24), we need the characters of the 6 matrices,

$$\chi(E) = 3 \; , \; \chi(\delta_3) = \chi(\delta_2^3) = 0 \; , \; \chi(\delta_{21}) = \chi(\delta_{22}) = \chi(\delta_{23}) = 1 \; .$$

Then, the left side of (5.24) becomes

$$1 \cdot 3^2 + 2 \cdot 0^2 + 3 \cdot 1^2 = 12 \; (\neq g = 6) \; .$$

Hence, this representation is reducible. With Equation (5.23) and Table 4.1 we obtain the numbers

$$\begin{aligned} n_{A_1} &= \frac{1}{6}(1 \cdot 3 \cdot 1 + 2 \cdot 0 \cdot 1 + 3 \cdot 1 \cdot 1) = 1 \; , \\ n_{A_2} &= \frac{1}{6}(1 \cdot 3 \cdot 1 + 2 \cdot 0 \cdot 1 + 3 \cdot 1 \cdot (-1)) = 0 \; , \\ n_E &= \frac{1}{6}(1 \cdot 3 \cdot 2 + 2 \cdot 0 \cdot (-1) + 3 \cdot 1 \cdot 0) = 1 \; . \end{aligned}$$

Hence, $\bar{\Gamma} = \bar{\Gamma}^A \otimes \bar{\Gamma}^E$.

7. As we have shown in Section 4.1.1, every representation is equivalent to a unitary one. Since the characters of two equivalent representations are identical, we can consider a unitary representation ($\tilde{\Gamma}^{-1}(a) = \tilde{\Gamma}^\dagger(a)$). Then, the statement follows immediately:

$$\chi(a^{-1}) = \sum_i [\tilde{\Gamma}(a^{-1})]_{i,i} = \sum_i [\tilde{\Gamma}(a)^{-1}]_{i,i} = \sum_i [\tilde{\Gamma}(a)^\dagger]_{i,i} = \sum_i [\tilde{\Gamma}(a)]^*_{i,i} = \chi(a)^* \; . \; \surd$$

8. If we choose the representations $p' = 1$ ($\Gamma^{p'}(a) = 1 \; \forall \; a$) and $p \neq 1$ in the orthogonality theorem (5.1) or (5.2), it then follows immediately

$$\sum_{a\in G} \Gamma^p_{i,j}(a)\Gamma^{p'}_{k,l}(a^{-1}) = \sum_{a\in G} \Gamma^p_{i,j}(a) = 0 \;\; . \;\; \surd$$

9. Because of Equation (4.20), the irreducible representations must be one-dimensional. Furthermore, according to Theorem 1, each element is its own class. Now, let G be non-Abelian. Then, there are at least two elements a, b with

$$a \cdot b = c \neq d = b \cdot a \; .$$

However, for some one-dimensional representation $\bar{\Gamma}^p$ it applies

$$\Gamma^p(c) = \Gamma^p(a) \cdot \Gamma^p(b) = \Gamma^p(b) \cdot \Gamma^p(a) = \Gamma^p(d)$$

i.e. the two different group elements c and d have the same character in each representation. This contradicts the orthogonality theorem (5.10) and therefore G must be Abelian. $\surd$

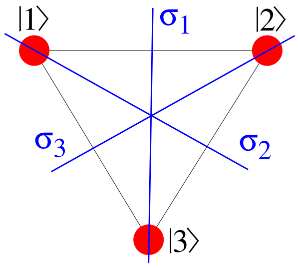

Figure B.6: A molecule with a triangular shape.

With this result, we can now apply the projection operators (6.14) to the state $\Psi(\vec{r})$:

$$\begin{aligned}
\hat{P}^A\Psi(\vec{r}) &= \frac{f(\vec{r})}{3}(\hat{T}_E \cdot x \cdot y + \hat{T}_{\delta_3} \cdot x \cdot y + \hat{T}_{\delta_3^2} \cdot x \cdot y) \\
&= \frac{f(\vec{r})}{3}\left(x \cdot y - \frac{x \cdot y}{2} - \frac{x \cdot y}{2}\right) = 0 \, , \\
\hat{P}^{E_1}\Psi(\vec{r}) &= \frac{f(\vec{r})}{3}(\hat{T}_E \cdot (x \cdot y) + \omega\hat{T}_{\delta_3} \cdot (x \cdot y) + \omega^2\hat{T}_{\delta_3^2} \cdot (x \cdot y)) \\
&= \frac{f(\vec{r})}{3}\left(x \cdot y + \frac{\sqrt{3}}{4}(\underbrace{\omega^2 - \omega}_{-\sqrt{3}\mathrm{i}})x^2 - \frac{x \cdot y}{2}(\underbrace{\omega + \omega^2}_{=-1}) + \frac{\sqrt{3}}{4}(\omega^2 - \omega)y^2\right) \\
&= f(\vec{r})\frac{\mathrm{i}}{4}(x + \mathrm{i}y)^2 \equiv \Psi_{E_1}(\vec{r}) \, , \\
\hat{P}^{E_2}\Psi(\vec{r}) &= f(\vec{r})\frac{\mathrm{i}}{4}(x - \mathrm{i}y)^2 \equiv \Psi_{E_2}(\vec{r}) \, .
\end{aligned}$$

Hence, we find

$$\Psi(\vec{r}) = \Psi_{E_1}(\vec{r}) + \Psi_{E_2}(\vec{r}) \, .$$

2. a) The group C_{3v} has the 6 elements $\{E, \delta_3, \delta_3^2, \sigma_1, \sigma_2, \sigma_3\}$ where the three mirror planes are displayed in Figure B.6. Like in Section 6.3.5, we can start again from the state $|1\rangle$ and construct a basis of the representation spaces of C_{3v} using the operators $\hat{P}^p_{\lambda,\lambda}$,

$$\begin{aligned}
\hat{P}^{A_1}_{1,1}|1\rangle &= \frac{1}{6}\left(\hat{T}_E|1\rangle + \hat{T}_{\delta_3}|1\rangle + \hat{T}_{\delta_3^2}|1\rangle + \hat{T}_{\sigma_1}|1\rangle + \hat{T}_{\sigma_2}|1\rangle + \hat{T}_{\sigma_3}|1\rangle\right) \\
&= \frac{1}{6}(|1\rangle + |2\rangle + |3\rangle + |2\rangle + |1\rangle + |3\rangle) \\
&= \frac{1}{3}(|1\rangle + |2\rangle + |3\rangle) \equiv \sqrt{3}|\Psi^{A_1}\rangle
\end{aligned}$$

where the state $|\Psi^{A_1}\rangle$ is normalized. For the 3 other operators we find

$$\begin{aligned}
\hat{P}^{A_2}_{1,1}|1\rangle &= \frac{1}{6}\left(\hat{T}_E|1\rangle + \hat{T}_{\delta_3}|1\rangle + \hat{T}_{\delta_3^2}|1\rangle - \hat{T}_{\sigma_1}|1\rangle - \hat{T}_{\sigma_2}|1\rangle - \hat{T}_{\sigma_3}|1\rangle\right) = 0 \, , \\
\hat{P}^{E}_{1,1}|1\rangle &= \frac{2}{6}\left(\hat{T}_E|1\rangle + \omega^2\hat{T}_{\delta_3}|1\rangle + \omega\hat{T}_{\delta_3^2}|1\rangle\right) \\
&= \frac{2}{6}(|1\rangle + \omega^2|2\rangle + \omega|3\rangle) \equiv \sqrt{3}|\Psi^E_1\rangle \, , \\
\hat{P}^{E}_{2,2}|1\rangle &= \frac{2}{6}(|1\rangle + \omega|2\rangle + \omega^2|3\rangle) \equiv \sqrt{3}|\Psi^E_2\rangle \, .
\end{aligned}$$

Because of our findings in Section 6.3.5, the Hamiltonian must be diagonal with respect to the three basis states $|\Psi^{A_1}\rangle$, $|\Psi^{E}_{1,1}\rangle$, $|\Psi^{E}_{2,2}\rangle$ with diagonal elements

$$\begin{aligned} \langle\Psi^{A_1}|\hat{H}|\Psi^{A_1}\rangle &= 2t \,, \\ \langle\Psi^{E}_{1}|\hat{H}|\Psi^{E}_{1}\rangle &= \langle\Psi^{E}_{2}|\hat{H}|\Psi^{E}_{2}\rangle = -t \,. \end{aligned} \tag{B.4}$$

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Note that Equation (B.4) confirms our general finding (6.23).

b) With the 3 states $|4\rangle$, $|5\rangle$, $|6\rangle$ we can define analogously

$$\begin{aligned} |\tilde{\Psi}^{A_1}\rangle &= \frac{1}{\sqrt{3}}(|4\rangle + |5\rangle + |6\rangle) \,, \\ |\tilde{\Psi}^{E}_{1}\rangle &= \frac{1}{\sqrt{3}}(|4\rangle + \omega^2|5\rangle + \omega|6\rangle) \,, \\ |\tilde{\Psi}^{E}_{2}\rangle &= \frac{1}{\sqrt{3}}(|4\rangle + \omega|5\rangle + \omega^2|6\rangle) \,. \end{aligned}$$

In the basis of the 6 states $|\Psi^{A_1}\rangle, \ldots, |\tilde{\Psi}^{E}_{2}\rangle$ the Hamiltonian is block-diagonal with 2×2 blocks of states $\{|\Psi^{A_1}\rangle, |\tilde{\Psi}^{A_1}\rangle\}$, $\{|\Psi^{E}_{i}\rangle, |\tilde{\Psi}^{E}_{i}\rangle\}$. The off-diagonal elements are

$$\langle\Psi^{A_1}|\hat{H}|\tilde{\Psi}^{A_1}\rangle = \langle\tilde{\Psi}^{E}_{i}|\hat{H}|\Psi^{E}_{i}\rangle = t' \,.$$

Thus, the Hamiltonian matrix has the form

$$\tilde{H} = \begin{pmatrix} 2t & t' & 0 & 0 & 0 & 0 \\ t' & 2t & 0 & 0 & 0 & 0 \\ 0 & 0 & -t & t' & 0 & 0 \\ 0 & 0 & t' & -t & 0 & 0 \\ 0 & 0 & 0 & 0 & -t & t' \\ 0 & 0 & 0 & 0 & t' & -t \end{pmatrix}$$

with eigenstates

$$\begin{aligned} |\Psi^{A_1}_{\pm}\rangle &= |\Psi^{A_1}\rangle \pm |\tilde{\Psi}^{A_1}\rangle \,, \\ |\Psi^{E}_{i,\pm}\rangle &= |\Psi^{E}_{i}\rangle \pm |\tilde{\Psi}^{E}_{i}\rangle \,. \end{aligned}$$

c) For l triangles, the Hamiltonian matrix is obviously block diagonal with l-dimensional sub-matrices. This corresponds to the problem of three decoupled one-dimensional chains with the Hamiltonians

$$\hat{H}^{\text{chains}} = \epsilon \sum_{i} |i\rangle\langle i| - t' \sum_{\langle i,j\rangle} |i\rangle\langle j| \,,$$

where $\epsilon = 2t$ or $\epsilon = -t$ and $\langle i,j\rangle$ is a sum over nearest neighbors.